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SYSTEM

OF

CHEMISTRY.

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SYSTEM

OF

CHEMISTRY.

IN FOUR VOLUMES.

BY

JOHN MURRAY, M. D.

FELLOW OF THE ROYAL COLLEGE OF PHYSICIANS, OF THE ROYAL
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SYSTEM

OF

CHEMISTRY.

THE substances which are formed in the Vegetable and Animal Systems are all compounds; and their chemical constitution is such, that they derive from it peculiar characters by which they are connected, and by which they are also distinguished from others.

In unorganised bodies the elements are generally united in binary combinations, and by the union of such binary compounds others are formed. In the products of the vegetable and animal systems, the ultimate principles are less varied; but there is more diversity in the modes in which they are combined: they exist generally in more complicated states of union, three, four, or more substances, having their affinities balanced, so as to form one individual combination; and from diversities in the modes of union, more than from differences in their ultimate principles, arise the differences of properties by which they are distinguished.

From this difference in constitution are derived other characters by which these orders of natural substances are discriminated. The compounds of the mineral kingdom, consisting, in general, of principles united by a single affinity, have no tendency to suffer spontaneous changes; or, when left to themselves, there is no cause to disturb the uniformity of their mutual attraction. That affinity too can in general be brought into action, and by presenting their principles to each other, we can effect their combination. We can analyse them with equal facility. We can therefore ascertain with accuracy their composition, both as to the nature and proportions of their constituent parts, and as to the modes in which these are combined. But the chemical characters of the vegetable and animal products are altogether different. As they consist of three or more principles, which have strong mutual attractions, the balance of these attractions, whence any particular compound exists, is easily subverted; the principles have a tendency to re-act on each other, and enter into new combinations,—a tendency rendered efficient by the slightest alteration of circumstances. Hence arises the facility of decomposition which is characteristic of these bodies: they are liable to spontaneous changes, fermentation and putrefaction: they are readily acted on by other agents, as by water or atmospheric air; and they are totally changed by an increase of temperature. As their principles, too, have mutual affinities of nearly the same force, they never escape insulated from a combination, but unite with each other, forming a complicated analysis; and as their composition, with regard to the ultimate principles, is much alike, the products of this analysis, in the different individual substances, are extremely similar. And, lastly, as we are incapable of balancing the attractions of the principles of which they are formed, or of placing them under the circumstances under which they were brought into union in the vessels of the animal or plant, we can seldom, by artificial arrangements, form compounds of a similar nature.

Such are the chemical properties which distinguish the products of organization,—their susceptibility of decomposition, the complicated nature of their analysis, and the similarity of its products, and the impracticability of their artificial formation by the union of their principles.

There are some subordinate distinctions between the vegetable and the animal substances. As the constituent principles of animal matter are more numerous, their affinities are more nicely adjusted, and more liable to be altered by alteration of circumstances: hence the animal products are, in general, more susceptible of decomposition. This, also, is different, with regard to the products, from that of vegetable matter; in particular, they are distinguished, by being liable to that species of spontaneous decomposition which constitutes putrefaction: the others decay, but their decomposition is not marked by the evolution of those products which distinguish that of animal matter, and which characterize this process. Their analysis by heat, too, affords different products. These differences arise principally from certain elements entering into the composition of animal substances, which are either not contained in vegetables, or, if present, are in inconsiderable proportion.

Though the compounds which belong to the vegetable and animal systems can seldom be formed by artificial arrangements, it is not to be concluded, as has been done, that this arises from peculiar unknown forces, from the exertion of which their natural formation has been accomplished. They are chemical compounds, the results of chemical affinities, which have been exerted merely under peculiar circumstances. We can even by artificial processes form compounds perfectly similar to some products of vegetation; and, although the actions by which the greater number of these products are formed can be only imperfectly imitated in our processes, we can still so far trace them, as to discover their theory, and the nature of the modifications to which they are subjected. Hence the natural formation of these substances is strictly a subject of chemical investigation: and vegetable and animal physiology, so far as it is connected with this, is a department of chemical science,—one which is at present the most defective and obscure, but in which the progress is perhaps the least limited, which may reach the highest perfection, and present the most important results.

If the law of definite proportions shall ever be found capable of being applied to the combinations of the elements of organic compounds, their chemical constitution will be determined with the same precision as that of inorganic bodies. The circumstances now enumerated as constituting the distinctions between these two classes, render this however extremely difficult, and have led to the opinion either that the application is impracticable, or that laws must be assumed to regulate the combinations of the one class, very different from those which regulate the combinations of the other. The view which I have illustrated in some parts of the preceding volumes,—that the definite proportions in which bodies unite are much more numerous than those which are obtained merely in insulated binary compounds, removes the principal difficulties on which these opinions rest. And there is perhaps no just reason to forbid the conclusion, not only that the law may be applied to organic compounds, but this even under the same modifications as those under which it is applied to inorganic matter. The subject will fall to be considered under the general observations on the composition of the Vegetable Proximate Principles.

BOOK IX.

OF VEGETABLE COMPOUNDS.

THE Vegetable Compounds being less complicated in their composition than those which are formed in the Animal System, and affording likewise, in general, the materials from which the latter are produced, are first to be considered.

Their chemical history may be comprised under three divisions. Under the first, may be stated the facts connected with their natural formation, or the principles of vegetable physiology, so far as this is dependent on chemistry. Under the second, may be considered in detail the chemical properties and relations of the several vegetable products. And to the third, will belong the consideration of their general analysis, and the chemical changes they suffer, either spontaneously, or when placed under peculiar circumstances.

CHAP. I.

OF THE FORMATION OF VEGETABLE SUBSTANCES, OR THE CHEMICAL PHYSIOLOGY OF VEGETABLES.

In entering on this interesting subject, it is necessary to give a concise view of the structure and functions of plants, at least in so far as these are related to the chemical processes carried on in the vegetable system, by which the numerous products of vegetation are formed.

The structure of plants is, in many respects, analogous to that of animals. Compared, indeed, with that of the higher orders of these, it is more simple: there are no organs corresponding to the brain and nerves, the heart, the digestive system, or the muscles; but even in the lower tribes of animals, all these organs are not uniformly present; and in the general frame of vegetables, we discover that arrangement which is in strict propriety named organized. There are solid parts through which vessels conveying fluids are distributed, and organs in which functions similar to those of animals are performed.

The organized structure of vegetables is best discovered in the larger and more perfect plants. These consist of a stem or trunk, which, at its insertion into the earth, divides generally, forming the root, and at its upper extremity terminates in branches, to which the leaves and parts of fructification are attached.

On making a transverse section of any of these solid parts, a difference of structure is observed. In the centre is a soft substance, which is named the Pith; external to this is the Wood, more hard and compact; and over the whole is an outer rough covering, the Bark.

The Bark is composed of three parts,—the epidermis, or external rough covering, consisting of numerous layers; the cellular tissue beneath, composed of fibres interlaced so as to leave interstices, which appear to be filled with a softer matter of a green colour; and the cortical layers next to the wood, and approaching to it in structure; and through these parts numerous minute vessels run. The Wood is denser than the bark. It is fibrous, and is composed of layers or zones, formed annually, and varying in density and size, as vegetation has been more or less vigorous. The wood next to the bark is softer, and has been named Alburnum. The Pith, or Medulla, in the centre, is softer, and more cellular: it is most abundant and most succulent in young plants; is diminished and nearly obliterated by age, and appears to be of little importance, as it may be extracted without injury to the plant.

Attached to the stem or branches, are the Leaves. Their structure is fibrous and interlaced, covered on each surface with a fine membrane, and having numerous vessels inosculating freely with each other. The superior surface is in general more smooth and shining than the inferior; the latter has more asperities. These surfaces perform different functions. By the under surface absorption principally is performed, as Bonnet established by numerous experiments *; water, or watery vapour, being taken in, when in contact with it; and vapour from the atmosphere, or dew, being probably absorbed in the natural situation. By the same surface, transpiration appears to be performed, as the experiments of the same author proved, and as has since been confirmed by Knight,—a plate of glass applied to the under side of a large vine leaf, in connection with the plant, being soon covered with humidity, while

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* Recherches sur l'Usage des Feuilles.

from contact with the upper part of the leaf, no portion of moisture appeared *. The upper surface appears principally destined to expose the fluid circulating through it to the chemical agency of light, and probably to emit the aërial matter arising from the decomposition of the circulating sap; and Ingenhousz accordingly found, that the leaves furnish an air containing more oxygen, when their upper, than when their under sides are exposed to light †. So well adapted are these surfaces to the performance of their respective functions, that when their position is reversed, the plant makes every effort to regain that which is natural to them. The leaves of some plants even follow the course of the sun, presenting always their upper surface to the direct rays of light. The importance of the functions the leaves perform, is sufficiently demonstrated by the fact, that when they are destroyed the plant soon decays and dies.

There is much difficulty in tracing the vessels of plants, their connections and terminations, and the course of the fluids they convey. Hence the different opinions that have been advanced with regard to them. Naturalists have agreed in distinguishing three kinds;—the common vessels, or those which convey the common juice or sap; the spiral vessels, which principally accompany these; and the proper vessels, or those which contain the peculiar juices of the plant after they are formed.

The first of these, the common vessels, occur chiefly beneath the cellular tissue of the root, stem, and branches, and rise longitudinally from the root to the leaves and flowers: they are discovered by immersing the root of a growing plant in a coloured vegetable infusion: it soon ascends in them, and may be traced to the leaf. Vessels

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* Philosophical Transactions, 1805, p. 278.

† Experiences sur les Vegetaux, tom. ii. p. 195.

apparently similar run from the epidermis in an oblique or horizontal direction.

The proper vessels are situated principally in the cellular tissue and internal bark: they appear to descend from the upper parts of the vegetable, and to convey a fluid downward. This is proved by the facts, that a coloured liquid does not ascend in them, as in the common vessels, when the root is immersed in it, and that, when the stem or a large branch of a plant is cut across, the proper juice issues from the upper margin of the incision. As the common vessels can thus be traced upwards from the root to the leaves, and the proper vessels convey a fluid in the opposite direction, it seems to follow, that the connection between them is established in the leaf. Darwin conjectured, that the central vessel, or bundle of vessels, which runs from the stalk to the apex of the leaf branching out in minute ramifications which communicate with each other, is formed by the union of smaller sap-vessels, and that it performs the office of a pulmonary artery, distributing the sap over the surface of the leaf, and exposing it to the chemical action of the air and light. From the extremities of the ramifications of this vessel, this fluid, thus changed, returns, he supposed, by other vessels which pass along the under surface of the leaf, unite at the footstalk, and form larger vessels, by which it is conveyed to other parts of the plant. He established this opinion by various experiments in which coloured infusions were found to rise from the stem, and to pass along the middle rib of each leaf, and into numerous branches to its extremity, upon its upper surface; in its progress it appeared to be changed into a milky fluid which returned by branches on the under surface; these forming into two large vessels, one on each side of the vessel in the centre conveying the coloured liquid, passed to the foot-stalk. The fluid prepared in this circulation through the leaf, Darwin supposed to be expended in the various secretions, and in the growth and nourishment of the plant *.

Mr Knight drew afterwards the same conclusions †. He found that when an incision is made round the stem of a plant, removing the bark, so as to cut off the connection of the stem by the medium of the bark with the leaves, it did not grow nor shoot out branches below the incision, but grew as usual above the incision, which appeared to prove that the sap rising from the root through the wood, is prepared in the leaves for assimilation, and returns by vessels descending through the bark, to be subservient to the nutrition of the plant. He farther endeavoured to trace the course of the sap into the leaf, and its return to the other parts of the plant. The sap-vessels are easily traced from the root through the soft wood to the young stalks; the object was, to trace them farther. Having placed the stalk of the shoot in a deeply-tinged vegetable infusion, he found that the coloured liquid passed up the pores of the wood into the leaves without having coloured the bark. He farther found, that the leaf is attached to the wood by tubes, or bundles of tubes, through which the infusion had passed. These tubes, which he considers as different from the common or sap-vessels in the alburnum, he named Central vessels: they begin below the leaf, and extend to its extremities, where they appear to terminate. Lying parallel with these vessels, are others which are colourless, and appear to convey a different fluid. They seem to return the sap to the tree: for when a leaf was cut off which had imbibed a coloured infusion, the native juices of the plant flowed from these vessels apparently unaltered, as Darwin had before observed. They descend through the inner bark, and extend from the extremities of the leaves to the roots.

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* Botanic Garden, Notes, vol. i. p. 450. 455.

† Philosophical Transactions, 1801.

In conformity to these facts, Mr Knight gives the following view of the circulation of the fluids in plants, the same indeed as had been before given by Darwin.

The sap is absorbed by the common vessels originating at the extremities of the roots, and rising through the alburnum of the root, stem, and branches; in the branches it passes into the central vessels, through them into the leaf-stalk, and ultimately into the leaf. There it is exposed, in the ramifications of these vessels, to the action of the air and light, and is converted into the proper juice of the plant: this is conveyed by the proper vessels which have their origin in the leaf, and unite and descend through the internal bark. In its progress through these it probably undergoes further changes, and is ultimately converted into the solid matter and various products of the plant *.

The use of the spiral vessels does not appear very obvious. They are always empty, hence some have supposed them to convey air: others suppose them to be absorbent vessels, and have accounted for this fact from their contractile power, in consequence of which they discharge the fluid they contain when cut. As they are found principally connected with the central vessels in the young shoots, and in any other part of the plant appear hardened and nearly obliterated, Mr Knight considers them as appendages to these central vessels, which facilitate the propulsion of the sap into the leaf.

In the general structure of vegetables now described, there exists a striking analogy to the frame of animals; and from this, as well as from the functions they perform, it has justly been inferred, that they are endowed with similar vital powers. At one period it was attempted to account for the motions of vegetables from their peculiar mechanism, independent of any living force; the ascent of the

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* Philosophical Transactions, 1801, p. 331.; 1803, p. 286; 1805, p. 160.

sap was ascribed to capillary attraction; and the movements of different parts of the vegetable were supposed to depend on the elasticity of their fibres. But such causes are altogether inadequate. Capillary attraction is insufficient to account for the motion of the sap; the velocity with which it ascends; the height to which it reaches; for its variable motion; its propulsion and discharge when the vessels are cut: or for the descent of the fluid in the proper vessels. Nor can the elasticity of the fibres of plants account for the spontaneous movements of their leaves and flowers, or of those motions which they perform when excited by external impressions. The similarity of these actions and motions in the vegetable system, to those performed in the animal system, for the attainment of similar ends, proves that they originate in a similar cause, and leads to the conclusion, that irritability, or the susceptibility of contraction from the application of external agents, belongs to the vegetable as well as to the animal system. From the structure of vegetables, and in particular the greater rigidity of their parts, its operation is not indeed so unequivocally perceived. But the functions they perform;—the absorption of external matter; the propulsion of the sap; the secretions whence new products are formed; the motions of their leaves; their susceptibility to the impression of external agents, light, heat, moisture, and electricity; their growth; and the formation and evolution of the embryo plant with similar powers; are phenomena inexplicable on any principles of mechanism, and obviously dependent on vital power. This power observes, even in its relation to external agents, nearly the same laws as animal vitality. The functions dependent on it require to be excited by the application of external agents; hence the necessity of the due application of heat, light, air, and water: if these are withdrawn, they languish, and the irritability of the plant accumulates; if they are applied in excess, it is impaired; and, lastly, if by a previous abstraction of the usual stimulants, the irritability has been accumulated, more vigorous action ensues on their re-application, or, if too suddenly and forcibly applied, an exhaustion of power takes place. The effects of soil, of moisture, of heat, light, and electricity, on plants; their sleep, germination, efflorescence, fructification, and decay, afford many beautiful illustrations of the operation of this principle, in conformity to these laws.

The preceding observations on the structure and moving powers of vegetables, lead to the consideration of the functions on which their growth is dependent, and by which, from new combinations, their products are formed.

Absorption takes place in vegetables, particularly by their roots. This absorption is not indiscriminate, otherwise plants should contain all the principles of the soil in which they grow. Neither is it pure water only that is absorbed, but water holding in solution or in suspension such substances as contribute to the nourishment of the plant. This is the source of the sap or common juice, which is found in different states at different periods. In winter it is in small quantity; in spring and summer it is more abundant; in autumn it becomes thicker and less copious; changes which may arise from the action of the sap-vessels, from intermixture of the proper juices, or from the solution of part of the solid matter through which it is conveyed. This last circumstance, Darwin supposed to have the most important influence. He supposed, that when vegetation is vigorous, as it is in the summer and commencement of autumn, nutritious matter is formed by the leaves, and is deposited as a reservoir of nutriment in the alburnum, or in herbaceous plants in the roots; that on the revival of vegetation in the spring, this is dissolved by the fluid absorbed from the soil, and serves for the formation of new buds and leaves. Hence, as he remarks, the leaves of the lower branches of trees are usually first expanded *. Mr Knight, who has stated the same view, found in conformity to it, that the sap in spring has a greater specific gravity, and possesses qualities indicating a quantity of matter to be dissolved in it, in a higher degree, as it is taken at a greater height from the root; while the wood of the stem or large branches, cut down in winter, has a greater specific gravity, and contains more extractive matter soluble in water, than the wood of the same species of tree cut down about the commencement of summer †.

The sap of different vegetables has been examined by Vauquelin. The sap of the common elm, (Ulmus campestris), he found to contain vegetable matter, acetate of potash, carbonate of lime, with slight traces of sulphate and muriate of potash, the vegetable matter being in larger proportion, as it was taken from the plant late in the season. The sap of the beech, (Fagus sylvestris), besides vegetable extractive matter, contained some tannin, gallic acid, and free acetic acid, without any carbonate of lime, but with a portion of acetate of lime. The sap of the birch with extractive, contained also saccharine matter, acetic acid, acetate of lime, and nitrate of potash ‡. Chaptal found in the saps of various vegetables, a quantity of vegetable extractive matter, having the characters of the matter which constitutes the ligneous fibre, which was slowly precipitated on standing either with or without the admission of the air, and which was also precipitated by acids, alkalis, and other re-agents ||. According to Mr Knight's observations, the sap always contains a large portion of air.

Not only is absorption performed by the vessels in the

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* Phytologia, p. 28. 52. 158. 165.

† Philosophical Transactions, 1805, p. 70. 101.

‡ Annales de Chimie, tom. xxxi. p. 20.

|| Memoires de l'Institut. National, tom. i. p. 288.

roots; it takes place also at the surface of the bark and leaves. Absorbent vessels run from the bark in a horizontal direction, and the fact of absorption by them is demonstrated, by the increase of weight which a branch from a tree gains by exposure to dew, or to a humid atmosphere.

Perspiration, by which a fluid or vapour is exhaled, counterbalances absorption. Numerous experiments prove its existence in vegetables. On placing a growing plant under a glass receiver, a fluid is soon condensed on the internal surface, which appears to be water, with a slightly odorous impregnation. The quantity perspired differs under various circumstances. It is increased by heat, by light, and by a dry atmosphere. In the experiments of Hales, a sunflower, three feet high, was found to transmit by transpiration, in twelve hours in the day-time, about twenty ounces of fluid. This function appears to be performed by the leaves, and principally by their under surface. There also exist numerous pores in the bark, through which, probably, a discharge of fluid takes place.

Respiration is another function which plants perform; they are at least affected by, and produce changes in the atmosphere, and in other aërial fluids. The nature of these, though it has been the subject of numerous experiments, is still imperfectly known; and the statement of this function, so important in relation to the chemical physiology of vegetables, requires some details.

Priestley, from some experiments, inferred, that plants growing in air vitiated by combustion or the respiration of animals restore its purity.. He afterwards investigated the subject more fully; and though the results of his experiments were variable, he found, that in many of them, when a plant, or the shoot of a plant, was placed in air which had been vitiated by respiration or the combustion of a taper, in which, of course, carbonic acid was present, while the oxygen was abstracted, in a few days the air had received an accession of oxygen gas; and, in some cases.

the proportion appears to have been increased to even more than the usual proportion in atmospheric air *. And, in subsequent experiments he found, that air containing a large proportion of oxygen was evolved from aquatic plants immersed in water, and exposed to solar light †.

This office, apparently performed by the vegetable kingdom, opened an admirable view of adjustment in the economy of nature. All the tribes of animals consume the oxygen of the air which they breathe, and form carbonic acid gas, which they expire; and the necessary effect of both these operations is to render the atmosphere less fit to support life. There must, therefore, be causes equally constant and general in their action by which this is counteracted, and the purity of the air preserved. This was supposed to be performed by the vegetable kingdom,—growing plants giving oxygen to the atmosphere, and absorbing from it, and decomposing carbonic acid. The one tribe of animated beings, therefore, appear opposed to the other in the changes they induce on the air which is indispensable to both; and, by these reciprocal changes, it is preserved in a state adapted to the support of each.

Priestley's experiments, however, were not uniform, and in many of them, the changes produced by vegetation in the air appeared to be even the reverse. He often found, that the vitiated air was not ameliorated, sometimes it was even farther injured; and in other experiments he found, that common air was diminished, and rendered noxious ‡. Scheele, in experiments made nearly at the same time, found that the purity of the air was always injured both by germination and vegetation: and he added the general result, that he had " preserved fresh roots, fruits, herbs,

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* Experiments on Air, vol. iv. sect. 28.

† Ibid. vol. v. sect. 2.

‡ Ibid. vol. iv. p. 299. 301. 321.

flowers, and leaves, each separately in a matrass, and found, after some days, one-fourth of the air changed into aërial acid *."

The evolution of oxygen by vegetables appeared on the other hand to be established in a series of experiments by Ingenhousz. He found that from the leaves of vegetables, from their green branches, or even from the entire vegetable, when placed under water and exposed to the solar light, oxygen gas is evolved †; and, as the result of his numerous experiments, he adopted the conclusion, that oxygen is elaborated in the leaves or other organs of vegetables, by a vital action excited and sustained by solar light ‡. This latter conclusion he supposed to be proved by the facts, that after a short time, the emission of oxygen ceased, from the vessels of the leaf losing, as he supposed, their vital powers; and that leaves which had been bruised gave out no oxygen, while the leaves of the same plant detached from it, but without this destruction of organization, gave oxygen, the other circumstances being the same. He however found, that when light is excluded, not only does the evolution of oxygen cease, but the plant, either in atmospheric air, or in oxygen gas, consumes oxygen and produces carbonic acid; and the general result of his experiments, as he announces it, is, that vegetables deteriorate the atmosphere, except when exposed to direct solar light ||.

These experiments were always liable, from the manner in which they were made, to the objection, that the oxygen evolved might be the product of the action of the solar light on the water; the vegetable matter affording a surface, which presented the water in a favourable manner

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* Experiments on Air and Fire, p. 150.

† Experiences sur les Vegetaux, tom. i. p. 22. 105. 276. &c.

‡ Ibid. tom. i. p. 45. 91.

|| Ibid. tom. i. p. 61. 251.; tom. ii. p. 49. 102.

to this action; and this appeared to be rendered probable by the fact ascertained both by Priestley and Ingenhousz, that the emission of oxygen is materially dependent on the kind of water in which the vegetable matter is immersed; being more abundant from well-water than from any other; more so from river-water than from rain-water; and less copious, as well as less pure, from stagnant water, or water that had been boiled or distilled. The evolution, also, in the same quantity of water, continued only for a limited time; though on removing the water, and adding a new quantity, the production of oxygen took place as before. These facts appeared to establish the conclusion, that the production of oxygen is not the result of any function of the living vegetable, but of the chemical action of the light on the water, or on the humid vegetable matter.

Yet there are also facts which appear to prove, that the leaf operates in consequence of its organic structure, and the actions connected with this. Thus, Ingenhousz found, that in exposing to solar light, in separate portions of the same water, living vegetables, or the leaf of a plant newly detached, and substances which might equally afford a surface on which the light might act, as pieces of silk or cloth, while the former afforded oxygen, the latter gave none [*]: the oxygen given out is purer when the upper surface, than when the under surface of the leaf is exposed to the light [†]: and a larger quantity of oxygen is given out from leaves in maturity and vigour, than from those which are feeble, and imperfectly developed [‡]. While the leaves give oxygen, the flowers and other parts of the plant deteriorate the air [||]: leaves which are dead, or have their organization destroyed, give out no oxygen [§]: and, lastly, the quantity of oxygen evolved is greater than can be derived from the air which water holds in solution; and the water surrounding the leaf, when the process had ceased, instead of being deprived of air, is saturated with it, sparkles when agitated, and gives it out when exposed to heat *.

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[*] Philosophical Transactions, vol lxxii. p. 426.

[†] Experiences sur les Vegetaux, tom. ii. p. 193.

[‡] Ibid. tom. i. p. 108. 316.

[||] Ibid. p. 67. 71. 269. 274.

[§] Ibid. tom. i. p. 127.

Some light is perhaps thrown on this subject by a fact announced by Sennebier, and confirmed by Woodhouse and Saussure,—that the production of oxygen depends partly on the carbonic acid which water contains. Priestley and Ingenhousz having remarked that the leaves of plants exposed to light in water which had been boiled, gave no oxygen gas, while, when placed in well-water, this gas is emitted, Sennebier endeavoured to discover, what circumstance attending the well-water favoured this production of oxygen; he supposed it might be a portion of carbonic acid contained in it, the decomposition of which afforded oxygen: he therefore impregnated water with carbonic acid, and compared the quantity of air given out, when leaves were exposed to solar light in this water, and in common water, or water which had been boiled. In the last, he found no air to be given out; in the common water, a little was evolved; and a much larger quantity was emitted from the water impregnated with carbonic acid: after a certain time, the impregnated water lost this superiority, and it lost it instantly when the carbonic acid was abstracted by boiling, or by the addition of lime-water; while, if a little acid was added, to disengage the carbonic acid from the lime, the power of furnishing oxygen was restored †. These facts have been confirmed by other authorities. Ingenhousz found, that vegetables submitted to solar light, under water which had been boiled strongly, yield no oxygen; but on impregnating partially this water with carbonic acid, oxygen is afforded in large

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* Philosophical Transactions, vol. lxxii. p. 454.

† Journal de Physique, tom. xli. p. 206.

quantity, and of great purity [*]: and Woodhouse found, that the air produced by the exposure of the leaves of plants to solar light in river-water, is principally nitrogen, while that from the same water with carbonic acid is oxygen of a high degree of purity [†]. It appears to be proved, therefore, that the production of oxygen, when leaves are exposed immersed in water to the solar light, depends principally on the decomposition of carbonic acid contained in the water.

A series of experiments by Rumford, gave results apparently unfavourable to the conclusion, that the production of oxygen depends on any function connected with the organization of the leaf: various inorganic substances, as silk, cotton, and linen, immersed in water, and exposed to solar light, gave out oxygen gas, some of them as largely and in as great purity as vegetables do [‡]. In these experiments, however, the air was not withdrawn until after several days; and Ingenhousz justly remarked, that the production of the oxygen might be from the peculiar green matter which is always generated when water is exposed to light with any vegetable or animal matter. Rumford himself indeed states, that the water acquired a greenish tinge; and that on examining it, he found, that this green matter had been formed: and where the evolution of air took place sooner than any matter of this kind was generated, it was found, with the exception, in one or two experiments of the air from raw silk, to be not oxygen, but "was much worse than common air;" and it was only after the fifth or sixth day, when the production of the green matter might have taken place, that the production of oxygen commenced. And in employing a substance, such as fine-spun glass, which could exert no chemical agency on the water, nor contribute to the production of this green matter, but merely afford a surface, whence the air contained in the water might be extricated by the agency of light,—very little air was extricated, and the small quantity obtained was rather worse than common air. These experiments, therefore, rather confirm than invalidate those of Priestley and Ingenhousz.

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[*] Experiences sur les Vegetaux, tom. ii. p. 282. 296. 408.

[†] Nicholson's Journal, 8vo, vol. ii. p. 157.

[‡] Philosophical Transactions, 1787, p. 84.

It is more satisfactory, however, to determine the changes occasioned in the surrounding air by a vegetable in its natural situation. This has often been the subject of experiment, but with results far from being uniform.

Priestley observed that air injured by respiration, or combustion, was ameliorated by plants growing in it *. Sometimes, indeed, it was rather farther injured; but in this case the plant confined in the air was growing in earth; and the action of the vegetable mould might have given rise to the result. In other cases, where he introduced the flexible shoots of plants, by bending them, into jars of air, the air was ameliorated †. He farther found, that plants did not flourish when their branches were introduced into oxygen gas; nor when they were confined in carbonic acid gas, either pure or mixed with atmospheric air. Dr Percival had observed, however, that carbonic acid gas, supplied to growing vegetables in a small proportion, was favourable to their growth ‡. And Henry *senior* had obtained the same result ||. Ingenhousz had remarked, that plants, confined in an atmosphere containing a portion of carbonic gas, decompose it, and convert it into oxygen gas, when exposed to solar light; but the *direct* application of this light is necessary for this; so that, when it is even partially admitted, the conversion does take place,

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* Experiments on Air, vol. i. p. 91.

† Ibid. vol. iv. p. 500. 505. 507.

‡ Manchester Memoirs, vol. ii. p. 346.

|| Ibid. vol. ii. p. 357.

and, in a dark place, oxygen is consumed, and converted into carbonic acid *. He farther observed, that air vitiated by respiration is restored to purity, by shoots or branches of plants being confined in bottles filled with it, and exposed to the solar light; and this happens without the presence of water †. The experiments of Sennebier correspond with these. He found, that the air inclosed with the branches of plants under glass receivers, placed over water, and exposed to the sun, was a little ameliorated; and was still more so, when the branches were removed during the night, and were renewed every day: and that when branches were exposed to the light in this manner in nitrogen or hydrogen gas, there was progressively an addition of oxygen ‡.

Dr Woodhouse, professor of chemistry at Philadelphia, confined plants in atmospheric air, exposing them at the same time to solar light. "Carbonic acid gas was generally formed; and whenever this circumstance happened, the purity of the air was diminished." The results were similar when they were confined in oxygen gas. But instead of considering these changes as arising from functions performed by the living plant, he concluded, that the production of the carbonic acid is from the leaves of the plant decaying, and the oxygen of the air uniting with their carbonaceous matter. He supposed even that carbonic acid is decomposed by the living leaf, its carbon retained, and its oxygen evolved. And in confirmation of this he states the experiment, that when leaves of plants are exposed to solar light in atmospheric air, having a quantity of carbonic acid mixed with it, the carbonic acid disappears, and the atmospheric air increases in purity. He found also, that leaves immersed in water containing carbonic acid, afford-

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* Experiences sur les Vegetaux, tom. i. p. 52. 265.

† Journal de Physique, tom. xxviii. p. 84. 88.

‡ Physiologie Vegetale, tom. iii. p. 257.

ed oxygen on exposure to solar light; while, if the water contained no carbonic acid, they afforded principally nitrogen. Hence he concludes, that in all cases where oxygen is produced by vegetables, it is derived from the decomposition of carbonic acid; and as little of this gas is contained in the atmosphere, he supposes that the vegetable kingdom can have little effect in preserving the purity of atmospheric air *.

Theodore de Saussure had also formed the opinion, that carbonic acid is decomposed by growing vegetables, and that this is the source of the carbon of the plant, and of the oxygen it evolves. Hence his experiments, in his extensive investigation of this subject†, were directed to establish the facts with regard to this; and in nearly all of them plants were exposed to atmospheric air, with an admixture of carbonic acid gas. When the proportion of this gas did not exceed a twelfth part of the atmospheric air, it proved favourable to vegetation, and the plant flourished more than in common air: when it exceeded this much, it was prejudicial; and in an air consisting of half of its volume of carbonic acid gas, the plants perished in seven days. Oxygen, he also found, must be present to admit of the plant receiving benefit from the admixture of carbonic acid gas. In the atmosphere, of which carbonic acid forms a part, the carbonic acid he found to be always consumed; its carbon enters into the composition of the vegetable matter, and part of its oxygen is expended in the same manner, while the remaining oxygen, with a small proportion of nitrogen, are exhaled.

Thus seven plants of *Vinca minor* were confined in a mixture of atmospheric air and carbonic acid gas, (the latter amounting to 7½ parts in 100), the roots of the plants being in a separate vessel, and were exposed six successive days to the direct rays of the sun. On the seventh day the air had suffered no alteration in volume; but in its composition it was entirely changed: lime-water gave no indication of any carbonic acid in it, while the proportion of oxygen amounted to $\frac{24\frac{1}{2}}{100}$; the original proportion being $\frac{21}{100}$. The quantity of carbonic acid gas, amounting to $21\frac{3}{4}$ cubic inches, had been consumed; if the oxygen of this had been all emitted, it would have occupied the same volume; but the quantity amounted only to $14\frac{3}{4}$ cubic inches; hence 7 cubic inches of oxygen, or about the half of that discharged, was retained by the plant and assimilated, while a portion of nitrogen gas (7 cubic inches) had been exhaled by it.

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* Nicholson's Journal, 8vo, vol. ii. p. 150.

† Recherches Chimiques sur la Vegetation.

From a comparative experiment, Saussure adds, he found that the seven plants of Vinca minor would have furnished, by decomposition, 9.95 grains of charcoal, previous to exposure to the atmosphere containing carbonic acid gas; while the same plants, after that exposure, afforded of charcoal 12.23 grains. These results were confirmed by a number of experiments on other plants, (Mentha aquatica, Lythrium salicaria, Pinus genevensis, Cactus opuntia), and the general conclusion drawn, that under exposure to light, plants decompose carbonic acid by their leaves, retain its carbon and part of its oxygen, the remaining oxygen with a portion of nitrogen being exhaled *.

It is this decomposition of carbonic acid, according to Saussure, which is the source of the carbon in plants, since, when made to vegetate in pure water and in an atmosphere deprived of carbonic acid, he found, that they increased in bulk without any addition of carbon, or with even a slight diminution of it. But in common atmospheric air, where a small portion of carbonic acid is supplied to them, he found, (in opposition to Hassenfratz, who had stated †, that plants vegetating in pure water,

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* Recherches, p. 42. 45.

† Annales de Chimie, tom. xiii.

and in atmospheric air, contain, after their growth, less carbon than before), that the proportion of carbon is augmented from this source. Thus the roots of Mentha piperita being plunged in bottles full of distilled water, and allowed to vegetate, under exposure to the air and light, it was ascertained by comparative experiments, that 100 parts by weight of the plants employed, contained 48.29 of dry vegetable matter, which afforded 10.96 of carbon; while after vegetating for 2½ months, the 100 parts had increased in weight to 216 parts, which dried weighed 62; and from these were obtained 15.78 of charcoal. A similar result was obtained, when beans were made to vegetate in pieces of flint, in a glass capsule, and supplied with distilled water. The original beans gave 22½ grains of charcoal: while, after vegetation in the open air for three months, the plants afforded 51 grains[*].

When light is not present, other actions are exerted. Carbonic acid, instead of promoting vegetation, is hurtful, and is not decomposed, or is decomposed only in minute quantity. In atmospheric air freed from carbonic acid, the recent leaves, when light is not present, consume a portion of the oxygen, and after a short time form carbonic acid gas[†]. This, if not removed, proves injurious, while the plant remains in obscurity. But if light be admitted, it is rather advantageous; the plant again decomposes it, retains its carbon, and emits its oxygen.

The summary view, therefore, of respiration performed by vegetables, and its connection with their growth, as given by T. Saussure, is, that plants under exposure to light, absorb and decompose carbonic acid, whether supplied by the atmosphere, by water, or from the soil; its carbon, and part of its oxygen, enter into their composition, and the remaining oxygen is given out. In darkness this oxygen, or the oxygen of the surrounding air, is again consumed; it acts on the matter of the plant, combines with its carbon, and forms carbonic acid, which is exhaled; on the return of light this is decomposed, its carbon and part of its oxygen are transferred to the plant, and its remaining oxygen emitted; and hence, if a plant be exposed alternately to light and shade, neither the volume nor purity of the air is altered *.

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[*] Recherches, p. 50. 52.

[†] Ibid. p. 64. &c.

A series of experiments was published by Mr Ellis †, which present a more simple view of the effects of vegetation on atmospheric air. They lead to the conclusion, not before, I believe, distinctly advanced,—that the function of respiration is, as to its results, the same in vegetables as in animals; that the former, as well as the latter, in all situations, consume the oxygen of the air, by converting it into carbonic acid.

It had been fully established by the experiments of Scheele and others, that, during the process of germination, oxygen is consumed and carbonic acid formed. Mr Ellis inferred from his experiments, that the same changes continue to take place in vegetation. Having allowed some seeds of mustard to vegetate on moistened flannel, until they had grown to the height of more than an inch, he introduced them into a jar of atmospheric air, supporting them by a small hoop with netting. Lime-water was placed beneath, and the mouth of the inverted jar was surrounded with water. In a few hours a thick pellicle overspread the lime-water: at the end of twenty-four hours it was turbid, and the water had risen half an inch within the jar: at the end of the third day it had risen nearly an inch: the plants now began to look sickly, gradually drooped, and by the ninth day fell down against the sides

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* Recherches, p. 91.

† Inquiry into the changes induced on Atmospheric Air by the Germination of Seeds, the Vegetation of Plants, and the Respiration of Animals.

of the jar. The residual air extinguished a taper, and rendered lime-water milky; its oxygen therefore had been consumed, and carbonic acid formed.

In subsequent experiments, the changes in the air were determined with still more precision, and were always found to be the same. Its oxygen was uniformly consumed and replaced by carbonic acid gas, the proportion of which was such, that there was on the whole little diminution of volume. Carbonic acid gas, Mr Ellis endeavours to shew, is not necessary to the growth of plants; since the plant dies when it is supplied with it, if oxygen be not present; and, on the other hand, it lives and flourishes as long as it is supplied with oxygen, though carbonic acid be abstracted from it. The results in Saussure's experiments, in which vegetation appeared to be interrupted, and even vegetable life destroyed, when carbonic acid was entirely abstracted from a growing plant, by inclosing lime in the atmosphere in which it is confined, he ascribes, with sufficient probability, to a deleterious action exerted by the lime; and the fact stated on the authority of Saussure, that the lime proved injurious only when the plant was exposed to sunshine, he supposes owing to its being in that situation more readily volatilized. The experiments which prove the emission of oxygen by the leaves of plants when immersed in water and acted on by light, he contends, are inconclusive, as the leaf in this situation cannot be supposed to perform its natural function.

I have repeatedly witnessed Mr Ellis's experiments, and been fully satisfied of their accuracy. They agree with those of Scheele, and in part with those of Woodhouse; but they are in opposition to those of Priestley, and in some parts are at variance with those of some other chemists. It is hence difficult to form a decided opinion on a subject, with regard to which experiments appear to be so liable to fallacy.

I had formerly supposed, that the results in these experiments, and in those of Scheele, with regard to the consumption of oxygen and formation of carbonic acid, might have arisen from plants being employed, the white and succulent stems of which are large proportioned to their leaves, it being only the green parts of plants that have the power of evolving oxygen. Mr Ellis has since, however, obviated this objection, by employing plants the shoots or stems of which with the leaves are entirely green, and has still found the results to be the same.

He has also justly observed, that it is established by the greater number of the experiments on this subject, that oxygen is given out by plants only when under direct exposure to the solar rays. When not placed in this situation, the changes are reversed; not only in darkness, or an obscure light, but even in the clear light of day, there is the consumption of oxygen and the formation of carbonic acid. This is the result of his own experiments, and of those of Ingenhousz, and it may be inferred from those of Saussure.

The question, then, comes to be, which of these changes is the result of the natural function of the plant, or which is most essentially connected with its growth. On this point Mr Ellis has justly urged, that as so many plants grow, and form their products without being directly exposed to the rays of the sun, and as at certain seasons, and many climates, the degree of this exposure is inconsiderable compared with their seclusion from it, we are led to the conclusion, that it cannot be essential to their growth, but that the function which they more usually perform, must be considered as that on which their vegetation depends. " All the experiments," he remarks, " although they were not made under a direct exposure to the sun's rays, were conducted in open rooms, where light had the freest access, and the plants assumed all the characteristic properties and appearances which were peculiar to them. It is likewise sufficiently evident, that even in our own climate, and especially in high northern latitudes, a vast number of plants live and flourish in natural situations, where the direct rays of the sun seldom or never penetrate; and yet in such situations they attain a state of perfect vegetation. How many hours, also, of our brightest days, and even how many entire days, are we deprived of the direct influence of the sun's rays, at the very season when vegetation is advancing with the greatest rapidity and vigour? If indeed this direct influence were essential to vegetation, many plants which we now behold would never be produced at all, and all the tribes of vegetables would experience such frequent and continued checks to their growth, that in our own climate at least, we could scarcely ever hope to see many of them attain to a state of maturity *."

This conclusion may be just, yet the subject is not free from obscurity; for the results of experiments are evidently discordant. There can be no doubt, but that plants under exposure to the solar rays, decompose carbonic acid, and convert it into oxygen; and although the observations of Mr Ellis with regard to the connection of this with vegetation are just, yet it must appear singular, that plants can, without injury, so change the state of the functions they exert, as at different times to produce changes so entirely the reverse of each other; and farther, that they should exist in greatest vigour, and form their products in greatest perfection, generally in those climates, and universally at that season, in which they have, from situation with regard to solar light, been exerting to the greatest extent, that very function with regard to the air, supposed to be least natural to them, or the reverse of that to which their economy is adapted, and which they usually perform. We have the difficulty, too, if we adopt this view, of accounting for the origin, (particularly in the case of plants growing when supplied only with water and

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* Farther Inquiries, &c. p. 47.

atmospheric air), not only of the carbon which makes part of their substance, but of the much larger quantity which must be spent in the formation and evolution of carbonic acid. And the experiments of Saussure, if they are to be admitted as accurate, appear to prove, that the decomposition of carbonic acid by plants is essential to their growth; for according to those already referred to, (page 24.), if the small portion of carbonic acid which atmospheric air naturally contains were removed, by washing with lime-water, the vegetable supplied with such air merely expanded, without any real addition of vegetable matter, while, when supplied with water and with atmospheric air in its natural state, the proportion of vegetable matter increased with its growth, proving therefore, that it had fixed the carbon of this carbonic acid. Lastly, the green colour of plants is an indication of their vigour and proper state. It is unquestionably produced by the action of solar light; and since it is also present in plants which are exposed only to diffused light, this is a proof that the operation of both is similar, though more slow in the one than in the other; that under both situations, therefore, the same function is going on, a function evidently connected with the healthy condition of the plant, and essential to it. The agency of diffused light must indeed be similar to that of concentrated light, though less intense; and if the identity of effect is not apparent in the experiment of plants exposed to it, this must perhaps be ascribed to the diminution of power in transmission through the vessel in which the plant is confined, or to other circumstances connected with the experiment.

In concluding this subject, it may be remarked, that the changes effected by plants on the surrounding air, are less considerable than have been imagined, and that, when supplied merely with water, they are not very perceptible. Hassenfratz inclosed the branches of growing plants in atmospheric air, the roots being either in water or in earth, and found, that though the plants grew, yet at the end of two months, the air remained unaltered in volume, and in the proportion of oxygen *. A similar result was obtained by Woodhouse, who remarked, that "when a plant in perfect health, growing in a soil which contains little vegetable or animal matter, is confined in atmospheric air, it will live a long time without producing any change in it." It is probably principally from the soil that plants derive their nourishment, and they are much less dependent than animals on the surrounding air. They require also a less supply of nutritious matter, as their growth is more slow, and they lose less by any excretion. There appears too, to be a greater diversity in plants than in animals with regard to their relation to the air, some affecting it slowly, others producing changes in it speedily, and some being injured by one gas in which others live sufficiently well.

A peculiar relation exists between the chemical agency of light on plants, and the production of their colours: when secluded from light they become white; when exposed to the solar rays they regain their green tint; and it is only from the green parts of plants that oxygen is exhaled under exposure to light. This has been well investigated by Mr Ellis. The white colour had been ascribed to the retention of oxygen, and the green colour to the redundance of carbon; but as Mr Ellis has remarked, the oxygen retained when plants are secluded from light, is not in the state of oxygen, but in that of carbonic acid; and it does not appear how carbon can produce the green colour. The changes he supposes to depend on the agency of acid and alkaline matter. Acids weaken or destroy colours, and this independent of communicating oxygen. The loss of colour, therefore, when plants are secluded from light, may be owing to the retention of carbonic acid; and ac-

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* Annales de Chimie, tom. xiii. p. 325.

cordingly he found that this acid destroys the green colour of a vegetable infusion. When the plant is exposed to light, the carbonic acid is decomposed, hence this agency of it is suspended; and not only is this favourable to the restoration of the colour, but it is further so, by allowing any alkaline matter with which the acid had been combined, to exert its action in producing the green tint. Hence, too, we perceive the connection between the evolution of oxygen, and the presence of the green colour. It is not that the green parts of plants are peculiarly adapted to afford oxygen, but that the parts affording it become green, the evolution of the oxygen arising from the decomposition of carbonic acid. The same view of the colours of plants depending on the agency of acid or of alkaline matter, he extends to the successive changes they undergo in different periods of their growth, and to the colours of flowers and fruits *.

Vegetables are capable of being acted on by other aërial fluids, and of acting on them; though, with regard to this, much diversity prevails among the experiments of different chemists. According to Scheele, they do not flourish in oxygen gas, but decay and die †: the same conclusion was drawn by Priestley ‡. Ingenhousz, on the contrary, affirms, that a plant confined in oxygen gas, and either exposed to the light or kept in a dark place, vegetates, and lives longer and is more vigorous than in a similar quantity of atmospheric air; and it lives still longer if the carbonic acid gas which it generates, when kept in darkness, be abstracted ||. The results of Saussure's observations agree, however, with those of Scheele and Priestley; as he found plants to flourish less when kept in the shade in pure oxy-

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* Farther Inquiries, &c. p. 109.

† Chemical Observations and Experiments, p. 156.

‡ Experiments on Air, vol. iv. p. 326.; vol. v. p. 15.

|| Experiences sur les Vegetaux, tom. ii. p. 10. 15. 21. 76.

gen gas, than in oxygen diluted with nitrogen or hydrogen, either from the immediate action of the oxygen, or from carbonic acid being formed [*]. There is reason to believe, that where oxygen has appeared injurious to vegetables, it is from this last cause, and that directly it is rather useful, and even necessary to sustain the functions of plants. This appears from plants dying when kept *in vacuo*, and from the effects of other gases upon them.

Priestley found, indeed, that plants grow in air injured by combustion or respiration [†]; but, in opposition to this, Ingenhousz affirmed, that nitrogen, hydrogen, and carbonic acid, prove injurious to vegetables. Young plants he found to be incapable of resisting their noxious operation, either in the shade or under exposure to light; and even when they have acquired more vigour, although they resist it for a few days under favourable circumstances, they at length decay and die [‡]. Carbonic acid gas appears, from his experiments, to be peculiarly injurious to vegetable life, if its noxious quality be not counteracted by exposure to solar light [||]. Priestley likewise observed, that carbonic acid gas is injurious to vegetables [§]; and even Percival and Henry, who contended for its utility, admitted, that it proved hurtful if in its pure state, or unmixed with oxygen. Hydrogen gas Priestley found to be less injurious; and by some plants, as the willow, he observed it to be absorbed, without injury, in considerable quantity [¶], —an observation confirmed by Ingenhousz [**]. According to the observations of Humboldt and others, hydrogen is even capable of supplying, to a certain extent, the place of light, and of enabling plants to retain their green colour, which they otherwise lose when light is excluded [*]. Saussure more lately investigated the influence of the different gases on vegetation. Nitrogen appeared to be incapable of sustaining it: the plant continued to grow for a certain time, indeed, from the portion of oxygen which its green parts exhale; but plants not possessed of such parts, or deprived of them, did not vegetate in nitrogen. In darkness, plants confined in it exhaled carbonic acid. The general results with regard to vegetation in hydrogen gas and in carbonic oxide gas, were nearly the same [†].

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[*] Recherches, p. 92.

[†] Experiments on Air, vol. iv. p. 305. 326.

[‡] Experiences sur les Vegetaux, tom. ii. p. 5.

[||] Ibid. p. 72.

[§] Experiments on Air, vol. iii. p. 303.

[¶] Ibid. vol. iv. p. 320. 330.; vol. v. p. 2.

[**] Experiences sur les Vegetaux, tom. ii. p. 303.; tom. i. p. 297

The roots of vegetables perform functions with regard to aërial fluids different from the leaves. They consume oxygen, and form carbonic acid [‡]. The stems and branches of plants confined in atmospheric air vitiate it either in the shade or under exposure to light, without changing its volume, as they replace the oxygen they consume by an equal volume of carbonic acid gas. The flowers of plants produce changes on the air similar to those produced by the roots and branches. They appear to exhale also a portion of nitrogen gas in the shade [||].

Secretion is a function performed by vegetables, and subservient to the formation of their products. Were the sap which they absorb merely changed by respiration and the action of light, one product only could be formed from it in each plant; but very different products are formed and deposited in different parts of the vegetable; and the formation of these must be regarded as depending on the action of the vessels, and therefore as arising from a function analogous to secretion in animals. The organs in which this is performed are not ascertained. The utricles, or those bundles of vessels found in the stem and other parts, have been considered as secreting glands; but this is not established by any proof. The secreted products constitute the chief proximate principles of plants.

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[*] Journal de Physique, tom. xliii. p. 595.

[†] Recherches, p. 194.

[‡] T. Saussure Recherches, p. 104. 109.

[||] Ibid. p. 116. 126.

After these observations on the functions of vegetables, we have to trace, as far as can be done, the operation of those substances which are received into the vegetable system, and those processes by which these are converted into the varieties of vegetable matter.

The seed of vegetables consists of two essential parts,—the Germ, or small bud, the part endowed with life, and the rudiment of the future plant; and the Cotyledon or Seed Lobes connected with it, forming often the principal substance, and which, in the first stage of the growth of the plant, appears designed to afford to it nutritious matter. In the germ two principal parts are discoverable,—the radicle, which descends from the seed, forming the root, and the plumula forming the stem; and it is connected with the substance of the seed by slender vessels, which ramify through it, and which unite at their connection with the germ. When the seed is planted in the ground, or placed in other situations favourable to its vegetation, it absorbs moisture, and swells; the radicle begins to shoot out, and, at the same time, the substance of the seed suffers a change in its qualities. This constitutes the vegetable function of Germination, the first stage of vegetation, and which, when performed on certain grains preliminary to fermentation, forms the process of malting. From its connection with these processes, it has been repeatedly examined, and the principal facts with regard to it have been determined.

In germination there is a conversion of the fecula of the grain into sugar; how this is effected is to be inferred from the chemical actions which are exerted during the process.

In the first place, the presence of oxygen is indispensible to germination. If seeds moistened are placed *in vacuo*, they do not germinate; as was long ago ascertained by Boyle. If they are confined in nitrogen gas, hydrogen gas, carbonic acid, or nitric oxide gas, or if they are placed over quicksilver, germination does not take place. When immersed in water from which the atmospheric air is excluded, they swell, and the radicle is formed,—but vegetation makes no farther progress. And in all these cases, if the seed has been moistened, the life of the germ is soon lost, the matter of the seed decomposes and becomes putrid, and a portion of gas, consisting of carbonic acid, with a little carbonic oxide or carburetted hydrogen, is disengaged. These facts have been established, by the experiments of Scheele, Achard, Ingenhousz, Gough, Cruickshank, Huber, and Ellis.

When atmospheric air or oxygen gas is admitted to the moistened seed, germination soon commences, the oxygen is consumed, and carbonic acid is formed. The germination is more rapid in oxygen than in atmospheric air, as Huber ascertained *. It was likewise found by Humboldt, that in seeds which, from having been long kept, did not germinate when moistened and exposed to atmospheric air, the germination commenced when they were moistened with water impregnated with oxymuriatic acid, which afforded oxygen to them in a more condensed state; and by the application of the same liquid, the germination of seeds in their usual state was accelerated †,—facts confirmed by Von Uslar ‡ and T. Saussure ‖. Huber found, however, that although oxygen gas accelerates germination, it proves prejudicial to the progress of vegetation, when the parts of the embryo plant begin to expand; and in twenty-four hours, it was necessary to re-

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* Mémoires sur la Germination, p. 19. 141.

† Philosophical Magazine, vol. i. p. 509.

‡ Observations on Plants, p. 158.

‖ Recherches, &c. p. 4.

move it, as otherwise the radicles became brown and decayed [*]. The presence of a little carbonic acid gas with the oxygen gas, he found rather useful, probably by diluting it; for in atmospheric air, germination is rather favoured if the carbonic acid be withdrawn as it is formed, as Saussure found; and a large proportion of carbonic acid gas was found by Huber to be hurtful, even when oxygen was present [†].

Scheele observed, that during germination, the volume of the air is not altered, the oxygen gas consumed being replaced by an equal volume of carbonic acid gas,—a fact also ascertained by Cruickshank and Saussure. As there is no change of volume when oxygen is converted into carbonic acid, this result seems to prove, that in germination no part of the oxygen is absorbed by the seed, or enters into combination with it, but that it merely abstracts carbonaceous matter. Some chemists, however, have been disposed to draw the opposite conclusion. Thus, Mr Cruickshank, from considering that carbonic acid is evolved from moistened seeds when oxygen is not present, as when they are placed in nitrogen gas,—a fact ascertained by his own experiments, and since by those of Huber [‡],—supposed, that the formation of this acid is owing to the decomposition of the water, the oxygen of which combines with carbon from the seed; that therefore, in germination, the same changes happen; and that the oxygen which disappears is in part absorbed, and enters, with perhaps a proportion of hydrogen from the water, into the composition of the saccharine matter formed in this process. This reasoning is not very conclusive; for admitting that water is decomposed by humid seeds, when oxygen is excluded, it does not follow, that this will happen when oxygen is present, exerting its chemical affinities.

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[*] Mémoires sur la Germination, p. 20.

[†] Ibid. p. 55. 75. 78.

[‡] Memoires, &c. p. 170. 175.

The question, with regard to this point, might be determined, by ascertaining whether seeds lose weight in germination, and whether this loss is exactly equal to the quantity of carbon which has been abstracted, estimating this from the quantity of carbonic acid produced. The determination of this, however, is difficult, from the difficulty of estimating the loss of weight which the seeds sustain from the exhalation of part of the water with which they have been moistened. Saussure states, that a seed, brought after germination to the same state of dryness as before, not only always weighed less, but the diminution of weight was even greater than could be accounted for by the carbon abstracted during the germination, and the small quantity of mucilage that might be dissolved by the water in which the seeds had been macerated. Thus, he placed a number of peas, weighing 200 grains, over mercury, with five times their weight of distilled water, in a jar, filled with atmospheric air. They germinated; and, at the end of two days, 4½ cubic inches of carbonic acid were formed, containing 0.85 grain of carbon; the water had dissolved a little extractive or mucilaginous matter, which was found to amount to 0.75 grain. The seeds, in drying, still continued to form carbonic acid, in quantity rather less than what was formed during the same time in germination; but assuming it to be the same, the seeds having required two days to dry, it followed, that in that time they must have formed other 4½ cubic inches of carbonic acid, or lost 0.85 grain of carbon. The total loss, therefore, amounted to 2.45 grains; and when dried, they ought to have weighed this less, had the change they suffered consisted merely in the abstraction of carbon; while, had they received oxygen, the loss must have been less, or there might have even been, on the whole, an increase of weight. The loss, however, was much greater, being not less than 11 grains [*]; a result which renders the whole experiment doubtful; for since the loss amounts to 8.5 grains more than what can be accounted for by the quantity of matter ascertained to have been abstracted, it proves, either that the experiment had been inaccurate, or that a quantity of water had been dissipated, which could not accurately be estimated.

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[*] Recherches, p. 16.

The experiment, to determine whether seeds lose weight by germination, had been before made by Mr Gough, in a manner less liable to fallacy. He placed 7 drachms 23 grains of steeped peas in a phial, the mouth of which was covered with a piece of clean glass, intended to condense the vapour that might arise from them, while the access of air was not prevented: at the end of one hundred and twenty hours, the peas were vegetating freely; and on weighing the whole, they were exactly their original weight *. If the carbonic acid into which the oxygen of the air would be converted by germination, escaped from the phial in this mode of making the experiment, the result appears to establish, that the germination of seeds is attended with little, if any, diminution of weight. Mr Gough observed, that if, during the experiment, he withdrew the air frequently from the phial, by inspiring it through a syphon, there was a diminution of weight, of not less than 2 drachms 5 grains when 1 ounce 3 drachms of steeped barley were operated on; owing, probably, to the watery vapour arising from the germinating seeds having been withdrawn. The subject requires farther investigation; for it is still somewhat uncertain, whether in germination, besides the abstraction of carbon by the action of the oxygen of the air, there is a decomposition of a portion of the water, and an addition, from this decomposition, of oxygen and hydrogen to the matter of the seed.

To favour the chemical changes which constitute this process, certain circumstances are necessary. A due de-

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* Manchester Memoirs, vol. iv. p. 516.

gree of humidity is essential, seeds which are dry not germinating. It probably operates, by expanding the dry substance of the seed, and condensing a minute proportion of the oxygen, thus approximating it to the matter of the seed, and favouring its chemical action. The humidity of the seed will also be favourable to the developement of the plant. A certain temperature is also essential to germination. Below the freezing point of water, no seeds vegetate; and the greater number require a temperature considerably higher. This is conspicuous in the germination of seeds commencing and proceeding with rapidity, when the genial warmth of spring succeeds the winter's cold; and likewise in the seeds of many plants not germinating in cold, as they do in warm climates. The heat probably both excites the vital powers of the germ, and favours the chemical changes of the seed. Lastly, light has an important influence in germination, not, however, in forwarding, but rather in retarding it. It has been long known, that in the process of malting, which is nothing more than germination conducted with a particular view, the admission of light is hurtful; hence it is always conducted in darkened apartments: and it has been repeatedly ascertained, by experiment, that germination is impeded by light. Ingenhousz remarked, that seeds exposed to the solar light either do not germinate, but die, or, if they germinate, the plants are extremely weak *. It has been imagined, that the light operates by the heat it excites dissipating the moisture; but any effect of this kind, except from the direct action of the solar rays, must be trivial. As light, by its chemical agency, is an antagonist to the combination of oxygen, and as this combination, with the carbon of the seed, is necessary to germina-

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* Journal de Physique, t. xxxviii. p. 90.
Experiences sur les Vegetaux, tom. ii. p. 23.

tion, it is probably to this operation that its influence is to be ascribed.

By the chemical changes which occur in germination, the fecula of the seed is converted into saccharine matter, or at least into a product which is sweet, and analogous to sugar. This saccharine matter appears to serve as nourishment to the infant plant; for, being soluble in water, it is capable, in solution, of being absorbed by the vessels of the radicle, which ramify through the substance of the seed: and thus, in the first stage of its growth, the plant has a supply of nutritious matter, independent of any external source. Mr Gough, who stated this view of the operation of germination in contributing to the growth of the plant, observes, that it is confirmed by some experiments by Malpighi, in which, when the germs of seeds were abstracted from the lobes, and planted in the earth, few of them grew, and those that did, grew very imperfectly. This experiment was also performed by Bonnet. The seed having been previously softened, by being kept humid, he cut the two bundles of fibres which connect the germ with the seed-lobes; he planted the germ in garden earth, supplied with water; the radicle was emitted, and at length the leaves; but the plants were so diminutive, that they could scarcely have been recognised, and they soon died *.

From the nature of the changes which thus occur in germination, and which are indispensable, as preliminary to vegetation, we can assign the theory of those operations on the soil, which constitute some of the principal practices of agriculture. When the ground is ploughed, its cohesion is broken: it is divided into loose particles; and hence, when the seed is sown, it is placed in the most favourable situation for vegetation: it is supplied with moisture, without being immersed in water: its temperature is in

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* Bonnet sur l'Usage des Feuilles, p. 239.

some measure kept uniform: the operation of light is partially excluded; and from the looseness of the earth that covers it, the atmospheric air finds access to it, and promotes the germination and commencing vegetation. When the fibres of the root expand, they meet with little resistance, and are equally supplied with water and air.

When germination has been accomplished, and a source of nutritious matter supplied, capable of being absorbed by the embryo plant, its structure begins to be developed, and its functions commence. The radicle first extends, penetrates the soil, and increases in length. The part of the germ named the plumula likewise extends, and rises from the ground to form the stem. And the other parts are successively unfolded, according to the nature and structure of the plant.

Its nourishment, after this first stage of its growth, is to be derived from without. This nutritious matter is received principally from the soil and from the surrounding air; and the first object of inquiry in the investigation of the theory of vegetation, is the relation subsisting between these and the growing plant.

The greater number of vegetables arise from the earth, and receive from it a large share of their nourishment. There were always, however, some objections to the view which supposed this to be its sole source; and when chemistry had advanced so far as to accomplish the vegetable analysis with some degree of accuracy, it was discovered, that the solid substance of plants, as well as their various products, are composed of principles very different from those contained in the soil.

It was sufficiently known, that many vegetables flourish and increase in bulk when supplied with water alone; and it had likewise been often ascertained, that if a plant be made to grow in a known quantity of earth, the earth after a certain period, during which the plant had increased greatly in bulk, is found to have lost little of its weight.

The celebrated experiment by Van Helmont appeared to establish this fact. He planted a willow weighing 5 lbs. in an earthen vessel filled with dried earth, which had been carefully weighed. The pot was sunk in the earth, covered with a plate of lead, and rain-water was occasionally conveyed to it through a tube of lead. At the end of five years, on removing the tree, it weighed 169 libs. while the earth in which it had been planted, on being dried and weighed, was found to have lost only 2 ounces of its original weight. A similar experiment was made by Boyle. The seed of a gourd was put into earth in a pot, and supplied with water; the plant which grew from it, in the course of a few months, weighed 2¾ libs. yet the earth had not lost sensibly in weight *. These experiments have been repeated and diversified by modern chemists. Duhamel caused plants to grow, by supplying them with water alone, and they flourished sufficiently well †. Tillet found, that wheat and other grains grew in river sand, in pounded quartz, or in mixtures of silex, argil, and lime: they produced seeds, which sown again produced new plants, and this for three successive years ‡. Bonnet found, that plants supported on moss, cotton, or paper, grew when supplied with pure water, and produced flowers and fruit equal to what they produced when growing in the soil. Mr Hoffman inclosed sprigs of Mentha crispa in phials filled with distilled water, and closed by a cement of wax: they continued to grow, new roots and branches were formed, until the whole of the water had passed through the plants; and on weighing they were found to have gained in weight ||. Boyle had before made this experiment, and had found, that in less than a month a sprig of mint growing in distilled rain-wa-

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* Boyle's Works, vol. i. p. 494. 495.

† Mémoires de l'Acad. des Sciences, 1748.

‡ Ibid. 1772, p. 229.

|| Von Uslar on Plants, p. 100.

ter, increased to nearly four times its original weight *. Braconnot more lately made a series of similar experiments, and found, that plants grow when their seeds are sown in lithrage, in sulphur, and in washed sand, on being supplied merely with water and atmospheric air †. Parasitic plants too, and those which are attached to stones and rocks, can derive their nourishment only from water and air.

These facts appear to authorise the conclusion, that air and water furnish the principal part of the food of vegetables, and that many can live and grow on these alone.

Previous to the discovery of the composition of water, it was difficult to conceive how it could be converted into the solid matter of plants. Much of that matter, indeed, consists of water; but it contains also other elements with which this water is combined, and which must bear a certain proportion to it. The discovery of the composition of water solved this difficulty; for as oxygen and hydrogen are the principal elements of vegetable matter, it was obvious that they might be derived from this source.

That water is decomposed in the process of vegetation, appears to follow from the fact already stated, as established by experiment, that when the leaves of vegetables are exposed to light, in contact with pure water only, they afford oxygen gas, and that this is connected with the action of the vessels of the leaf. It has appeared, indeed, from the researches of Sennebier and Woodhouse, that the production of oxygen in this experiment, is considerably dependent on the quantity of carbonic acid contained in the water, or that at least by increasing the quantity of this acid a larger quantity of oxygen is evolved. It cannot, however, be affirmed to depend solely on this, for the decomposition of water is just as likely to take place as the

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* Boyle's Works, vol. i. p. 621.

† Nicholson's Journal, vol. xviii. p. 17.

decomposition of carbonic acid; both probably take place, and bear a certain relation to each other. That the oxygen evolved is in part derived from the decomposition of water, appears from this, that the portion of carbonic acid in common water is so inconsiderable as not to be appreciable; yet leaves exposed, immersed in such water, to solar light, afford oxygen. Ingenhousz found also, that though in boiled or distilled water the quantity emitted was less than in spring water, yet still a portion was evolved, and the apparent difference in the proportion was in part owing to the boiled water absorbing part of the air emitted *. This air was also purer oxygen than the air from spring water. The results of these experiments, added to the consideration, that, from no other source than from the decomposition of water, can the origin of the hydrogen contained in plants which grow when supplied with water and air alone, be derived, afford apparently satisfactory proof, that water is decomposed in the process of vegetation.

A due supply of air is also necessary to the growth of plants; but its agency in promoting the process is not equally obvious. It has been believed to operate principally by affording carbonic acid, which the vegetable absorbs, and the decomposition of which is the source of the carbon of vegetable matter; and in plants which grow when supplied only with air and water, there is no other obvious source whence this carbon can be derived. It appears accordingly to be established by the experiments, already referred to, of Sennebier, Saussure, and others, that in an atmosphere composed partly of carbonic acid, the leaves of plants absorb a portion of it, and convert it into oxygen. Saussure too found, that plants growing in pure water, and in atmospheric air containing its usual portion of carbonic acid, increase their quantity of carbon, which

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* Philosophical Transactions, vol. lxxii. p. 426.

they do not do if the carbonic acid has been previously abstracted. The uncertainty of our knowledge of the real changes which plants produce in the atmosphere, throws, however, some doubt on this subject; for if (unless when exposed to the solar rays) they consume oxygen and exhale carbonic acid, this view cannot be adopted; and we have even the additional difficulty of accounting for the source of the carbon contained in the carbonic acid they discharge.

The influence of the other principles of atmospheric air in promoting vegetation, is less clearly established. That of the nitrogen appears to be negative; that of the oxygen is more doubtful, and must remain so until it be determined which is the natural function of vegetables connected with their growth,—whether the consumption of oxygen and formation of carbonic acid, or the decomposition of carbonic acid and evolution of oxygen.

Whichever of these changes is produced by the leaves of plants, it appears, however, to be established, that the oxygen of the air is absorbed by the roots. There are experiments which prove, that plants grow mere vigorously when supplied with water impregnated with oxygen, than when common water is used *. T. Saussure found, that when the roots of plants are exposed to carbonic acid gas, to nitrogen, or hydrogen gas, they die in thirteen or fourteen days, while, when exposed to atmospheric air, they continue to flourish; and they consume the oxygen of the air in a quantity equal to their own volume, and form carbonic acid. When the roots were not detached, but remained in connection with the stem and branches placed without the jar in which the roots were confined with atmospheric air, they absorbed many times their volume of oxygen gas, which appeared to be conveyed through the plant, and delivered by the leaves to the external air. Saussure concludes, that the contact of oxygen with the

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* Philosophical Magazine, vol. i. p. 109. 224.

roots, is useful to vegetation. Hence many plants require a loose soil, and are more vigorous when their roots are not covered with too much earth *. But whether the advantage derived from oxygen thus applied, is from the stimulus it communicates to the vessel of the plants, or from its chemical agency, is uncertain.

From the facts that have been stated, it appears, that air and water furnish the largest portion of the food of plants, since so many grow when supplied with these alone.

In the chemical changes, however, which proceed in the vegetable system, the influence of another agent is indispensable. This is light. When it is excluded, plants become pale and feeble, their usual products are not formed, and they gradually decay. It is not by the heat which light excites that it is favourable to vegetation, for the same effects are not obtained when heat is applied without the admission of light. It may operate partly as a stimulant in relation to the irritability of the vegetable, exciting its vessels to increased action; but this cannot be its sole operation, as the substitution of other powerful stimulants ought, for a time, and to a certain extent, to be productive of the same phenomena, which is not the case. It must in part operate as a chemical power, and this chemical agency appears to be exerted in promoting the decomposition of carbonic acid, and the evolution of oxygen. How far this is connected with the process of vegetation, must remain uncertain, until it be determined, whether these changes, or the reverse changes of the consumption of oxygen and formation of carbonic acid, are those on which the formation of vegetable matter and the growth of the plant depend. The action of light is exerted principally on the sap circulating in the leaves; and when vegetables which have been blanched by seclusion from light are again exposed to it, the green colour appears first to-

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* Recherches, p. 104. 109. 111.

wards the margin of the leaf. It is in the leaf, therefore, that the principal chemical changes, from which the formation of vegetable matter arises, take place. It is well adapted by its position, to admit of the agency of light; and its structure is probably sufficiently porous to admit of the passage of those aërial fluids, which it either absorbs from the atmosphere, or evolves as the result of the decompositions which happen in the fluid circulating through its minute vessels.

VEGETATION is presented to us under the simplest point of view, when it is thus considered as connected solely with changes effected by the powers of the plant, aided by the chemical action of light on the water and air supplied to it. Many chemists, however, have called in question the conclusion, that vegetables grow when supplied with air and water alone: they have endeavoured to shew, that the experiments whence it is deduced are liable to fallacy, and that though there may be an enlargement of size or developement of parts, this is not perfect, and there is no increase of vegetable matter.

Hassenfratz stated these objections to the experiments of Van Helmont, Duhamel, and Tillet, and gave the results of experiments on various plants which expand when supplied with water, as hyacinths, kidney-beans, cresses, and others. They grew in this situation; but this growth was imperfect; the vegetation advanced no farther than the production of the flowers, without the seeds being formed, or at least without their coming to maturity; and when dried and analysed, the plant afforded, as he states, rather less carbon than was contained in the seed or bulb from which it had been reared *.

Experiments with a similar result have been made by T. Saussure. He endeavoured to bring into a state of vege-

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* Annales de Chimie, tom. xiii. p. 185. 188.

tation the seeds of the kidney-bean, the common pea, cresses, and similar plants, by supporting them on fine sand, and supplying them with distilled water. They frequently flowered, but their seeds never came to maturity [*].

Mr Knight has also observed, that bulbous and tuberose rooted plants contain the matter which serves for the developement of their parts; and that when they grow on being supplied with water, the water, if perfectly pure, operates, not by supplying them with new matter, but only by dissolving and distributing through the expanded plant, that which had been contained in the root [†].

To the experiment of a plant growing when supplied with air and water alone, it is farther objected, that in the period requisite to the growth of the plant, the water with which it had been supplied must have conveyed a quantity of foreign matter. Thus Bergman remarked, that even rain-water, with which the willow in Van Helmont's experiment was supplied, contains a small portion of earthy matter, which, by the constant supply, would accumulate in the plant in quantity sufficient to afford all the earth it contained at the termination of the experiment [‡]. And Kirwan remarked another source of fallacy, that the pot containing this willow being earthen, and of course porous, and being placed in the soil, a quantity of water from the soil, and conveying matter from it, must have precolated the vessel, and been absorbed by the roots of the tree [||]. A similar source of fallacy, it has been observed by Hassenfratz, existed in the experiments of Tillet [§].

These observations may prove, that plants supplied with water alone will not grow, that to some plants the supply both of air and water is even insufficient, and that these are incapable of vegetating properly, without matter derived from the soil. But they are altogether insufficient to render this conclusion general, or to invalidate the opposite conclusion, that vegetation may be supported by air and water alone, and that many plants supplied with these will flourish, and form their peculiar products.

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[*] Recherches, p. 245.

[†] Philosophical Transactions, 1805, p. 97.

[‡] Opuscula Physica, vol. v. p. 92.

[||] Essay on Manures, p. 30.

[§] Annales de Chimie, tom. xiii. p. 187.

Independent of the particular experiments already stated, the facts which establish this last conclusion are numerous, and on a scale which scarcely admits of any fallacy. It can scarcely be doubted, when we consider the circumstances connected with the growth of a large vegetable, as of any of our common trees. Their roots stretch to no great extent in the soil, and that soil does not require to be renewed, or to receive any supply of manure. Nay, frequently the situation is such, that scarcely any nutritious matter is afforded, or any thing but a support by which the plant is exposed to the air, and occasionally supplied with water, as in the example of those trees which grow from the crevices of a rock, frequently on the very face of a precipice. Yet, in these situations, the growth of the tree advances, its solid matter increases, and, in many of them, much vegetable matter is annually lost in the fruit, or the fall of the foliage. It is obvious, that the portion of soil with which the plant can be supposed to communicate, could not have contained the matter from which this increase is derived; and there is no external supply but from the atmosphere, and from water. We are reduced, therefore, to the conclusion, that from these the carbon, hydrogen, and oxygen, which form not only the basis, but almost the entire substance of the vegetable, must be derived.

It may be true, that in the experiment of Van Helmont, and others of a similar nature, a small portion of saline and earthy matter may be conveyed by the water to the plant; and this may be the origin, in whole or in part, of the saline matter which it would contain. But to many of the experiments, this objection does not, from the manner in which they were performed, apply, as, for example, to those of Bonnet, Hoffman and Braconnot, already referred to; and even in the experiment of Van Helmont, the supply of nutritious matter by infiltration could not be considerable; it must have existed in limited quantity in the soil itself; and the communication could not have been so extensive, as to have afforded from this source all the principles which formed the substance of the plant, and which increased it from five pounds to one hundred and sixty-nine pounds in weight.

Lastly, the experiments of Saussure already referred to (page 24.) are conclusive, in opposition to those of Hassenfratz, in proving, that plants acquire an augmentation of vegetable matter, when supplied with air and water alone. If the atmospheric air, indeed, were excluded, or rather, if the carbonic acid which it naturally contains were removed, by washing with lime-water, the vegetables expanded, without any addition of vegetable matter; but, when supplied with water, and with atmospheric air in its natural state, and exposed to light, the proportion of vegetable matter increased with the enlargement of bulk. The opposite results obtained by Hassenfratz were probably owing to the plants not having been sufficiently exposed to light; for, in this case, Saussure found, that the proportion of carbon is rather diminished than increased.

The two series of facts on this subject which appear opposed to each other,—the one proving, that many vegetables will grow when applied with air and water alone, —the other equally proving, that, in such a situation, the growth is imperfect, and is little more than an expansion of their solid matter, may perhaps be reconciled, by considering vegetation under the following point of view.

In plants which expand rapidly, as in those which were the subjects of the experiments of Hassenfratz, or of the observations of Knight, the contact of a rich soil may be necessary to bring them to perfection. The developement of their parts may so far exceed the slow supply of principles which they can assimilate from air and water, that they will decay before their vegetation is completed. But this only proves, that, from the nature of these plants, the expansion of their parts is more rapid than the supply of nutritious matter, under such circumstances, can support; though in others, the growth of which is more slow and gradual, a sufficient supply of nourishment may be derived from these alone.

In vegetables of this last description, under which are probably to be classed all the larger plants, a due proportion in the supply of water and of air will no doubt be required. Water alone can furnish only oxygen and hydrogen, and these, without a due proportion of carbon, cannot be accumulated in the plant; and, for the same reason, an excess of carbonic acid, or any other substance affording carbon, may not be of utility, as it must equally be incapable of being assimilated without the necessary proportions of the other two elements. In those plants which grow slowly, the growth will probably adapt itself, in establishing these proportions, to the quantities of each which are afforded to it; and thus air and water may afford the elements whence their products are formed.

It is equally true, however, that, in many vegetables, these are insufficient, and a supply of more nutritious matter is indispensable to their proper growth. This is proved by the most familiar facts in agriculture. Many vegetables will flourish only in certain soils. Those which require a rich soil, vegetate feebly in a poorer, and they always exhaust that in which they grow, so that it requires to be renewed by certain additions, consisting chiefly of decomposing vegetable and animal substances; and the decomposition of these so as to afford a more rapid supply of nutritious matter, requires even often to be accelerated by other agents, particularly by the operation of lime.

In conformity to the view of vegetation which I have just given, it follows, that those plants which grow rapidly must be those that will require these conditions; and that of such as grow more slowly, those will most require a large supply of nourishment which give the largest produce of seeds or fruit, compared with the plant when these begin to be formed. Those plants accordingly, which are cultivated for the nourishment of animals, are those which demand the most nutritious soil, and the most stimulating manures; and the quantity of their products is within some limits proportioned to this. It is interesting to trace the operation of the substances from which these results are obtained.

The matter thus required by many vegetables to enable them to grow and form their various products, must be such as contains the elements of these products, and, at the same time, such as they can absorb and assimilate. Hence the great superiority of decaying vegetable and animal matter. This constitutes the richness of a soil: the earthy matter consists principally of silex, argil, lime, and magnesia: according as one or other of these predominates, and according to the state of aggregation in which they exist, the soil may be loose, or adhesive; retain warmth, or by hygrometric action attract moisture; may be calculated to retain water, or to allow it a free passage; or may have other qualities influencing the growth of plants, and, from such qualities, may be adapted to the support of certain vegetables. But in sustaining those plants which are cultivated for the nourishment of animals, something more is required: it must contain decomposing vegetable and animal matter: its fertility ceases when this has been abstracted, and can only be renewed by a fresh quantity being introduced.

This, therefore, forms the first and most important of the manures. Its nature varies according to the intermixture of animal and vegetable substances; but it must always contain, in large quantity, the elements of which vegetable matter is formed. The black mould into which vegetable matter passes by slow decomposition, and which always exists more or less in the soil, consists principally of the carbon which is the basis of that matter, with portions of the other elements. Saussure, in analysing it by heat, found it to contain more carbon and less oxygen than unchanged vegetable matter. It appeared to contain also a larger proportion of nitrogen. To water it yields a portion of extractive matter, and a small quantity of carbonic acid; and exposed in a humid state to the atmosphere, it absorbs oxygen, and forms carbonic acid *, as Ingenhousz, Gough, Humboldt, and others, had before observed.

The great utility of vegetable and animal substances as manure, consists in affording matter already assimilated, and hence more fit for the nutrition of the vegetable. The water present dissolves the mucilage and extractive principle, and, being absorbed by the roots, must afford more nutritious matter than water that is pure. Saussure found, that water holding in solution various salts, as well as different vegetable substances, gum, sugar, &c. enters the roots of plants by absorption; and that this absorption is in some measure elective, some substances being more largely absorbed than others. The salts thus introduced were afterwards discovered in the plant, on burning it †.

Not only is nutritious matter conveyed from the soil by the medium of water, but the gases evolved in the slow decomposition of the vegetable and animal matter mingled with it—carbonic acid, carbonic oxide, and carburetted hydrogen gases, are probably in part retained by the water of the soil and conveyed by it, and are also perhaps directly absorbed by the vessels of the root. Mr Knight

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* Recherches, p. 162.

† Ibid. p. 252. 260.

remarked, that in his experiments on the sap of vegetables, it always appeared to contain a large portion of air.

The quantity of vegetable matter directly conveyed into the plant, would appear, however, from Saussure's experiments, not to be considerable. He found, that rain-water, which had stood many days in a soil containing much manure, formed an infusion, which did not contain above one part of vegetable matter to a thousand of water. He found reason to conclude, too, that a plant, in absorbing this solution, would not assimilate above the fourth part of the vegetable matter it contained: hence, it would not increase in weight above a quarter of a pound, from the accession of this matter, in absorbing one thousand pounds of such an infusion, which, in a small plant, would require a very long time[*]. Braconnot has concluded, too, that black vegetable mould affords little directly nutritious to vegetables, as he found it communicated no soluble matter to water, and that, according to the opinion suggested by Parmentier and Tillet, it is useful principally by retaining moisture[†]. The result of his experiments, however, is at variance with that of Saussure, and is indeed not very probable in itself; and with regard to the conclusion of both chemists, it is to be remarked, that, independent of the matter directly afforded by manures to the water in the soil, much of the nourishment they afford to the plant is probably by the medium of the gases they evolve.

It may be affirmed, that vegetable and animal substances furnish the only species of manure directly nutritious, that is, matter which the vegetable can assimilate. But there are others, scarcely less useful, in improving the soil, in promoting the decomposition of the vegetable or animal substances which it contains, or in exciting the plant to more vigorous action.

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[*] Recherches, p. 267.

[†] Nicholson's Journal, vol. xvii. p. 16.

Of these, the first place is due to lime. Its utility is sufficiently known, not only in increasing the products of vegetation, but in improving their quality; and various opinions have been offered on its mode of operation. In clay soils it may prove useful, by rendering the earth more free and loose, more pervious to air and moisture, and to the roots of plants; it may likewise destroy insects, which prey on the tender vegetable: it may decompose any saline substance injurious to vegetation; and it probably acts as a stimulus to the plant arrived at maturity, and quickens the process of vegetation. But the principal advantage attending the use of lime as a manure, appears to be derived from its power of hastening the decomposition of vegetable and animal substances, and thus applying to the plant in greater abundance the different gases capable of contributing to its nourishment. That lime does exert such an operation, is evident from its reducing even the ligneous matter of plants in a short time to a black mould, when its action is favoured by humidity; and that it is by this operation that it proves useful as a manure, appears to be established by the fact, that its utility is most conspicuous in those soils which abound in animal and vegetable matter; and when this is exhausted, the lime is less useful, until it is renewed. It operates in producing this decomposition, probably not by combining with the vegetable or animal matter, and entering with it into the vessels of the plant; for it cannot well be supposed, that so much lime as must thus be conveyed, could be received without injury into the vegetable system; but principally by a resulting affinity, causing new combinations of the elements.

Lime, united with carbonic acid, has an effect similar, though in an inferior degree; and, united with sulphuric acid, under the form of gypsum, it has been used with advantage as a manure, probably from an analogous operation. Even some saline substances have been found to promote vegetation, such as muriate of soda, when added in very small quantity. Duhamel found, that marine plants growing in an inland situation languish, if not supplied with this salt.

The nature of the soil, too, with regard to its earthy and even its metallic ingredients, has an important influence on vegetation, and adapts it to different plants, partly perhaps from the elements these substances may afford, but chiefly from their mechanical effect in rendering the soil more or less pervious to the roots, in enabling it to afford to the vegetable a more or less firm support, and admitting the application of air and water in due proportion ; in absorbing water from the atmosphere by hygrometric attraction ; and in absorbing and retaining heat. The earthy matter of the soil is derived from the disintegration of the rocks over which it lies, or from materials originating from such disintegration, and spread over the surface by the operation of water. It must consist, therefore, of the principles of which the earthy aggregates are formed, and, in different situations, will consist of these in different proportions. Of the earths, silex and argil constitute the basis of every soil ; and the qualities of this mixture vary, according as either predominates. A soil in which argil is the chief constituent, or which consists principally of clay, is stiff, and not easily worked: it imbibes water, so as to be thoroughly moistened, very slowly ; but when brought into this state, it retains it strongly, and in drying it contracts and hardens, so as not to admit easily of the extension of the roots of plants, or be very permeable to water and air. Silex seldom exists in large quantity in a soil in a state of fine division, but in fragments, forming a sandy or gravelly soil. In this, qualities the reverse of those of a clay soil prevail : and hence the adaptation of each to particular plants, as well as the advantage derived from a due proportion of the one to the other. The presence of calcareous earth serves, to a certain extent, the same purposes : it lessens the adhesive quality of the clayey soil, and the porosity and looseness of that in which silex predominates; and probably is farther useful, in stimulating the vessels of the root, in attracting carbonic acid, and in favouring the decomposition of inert vegetable matter. Magnesia is probably always present in very inferior proportion, and its operation does not appear to be well marked: though it has been concluded, that when it is in excess it is rather hurtful to vegetation, from some kinds of limestone, which contain magnesia, being found to be prejudicial when used as manure. Oxide of iron is the principal metallic matter present in the soil; and it has been supposed to be in some cases advantageous, by attracting oxygen from the atmosphere.

An extensive series of experiments, on the comparative powers of different mixtures of earths in sustaining the vegetation of those plants which are cultivated for nourishment, was undertaken by Tillet *. He employed large earthern pots, which he sunk in the earth nearly to the level of the surface, so that the plants growing in them might be as much as possible in a natural situation, and participate in all the vicissitudes of the season; and, with the same view, he abstained from supplying them with any water, even when, from the want of rain, they seemed most to require it. The experiments on each earthy mixture were continued for three successive years; the grains produced the first year being planted for the second, and those produced the second being in like manner planted for the third. From their general results, it appears, that there is a considerable latitude with regard to the earthy mixtures capable of supporting vegetation. Wheat was the grain that was the subject of experiment; and it was found to grow well in various mixtures of sand, clay, plaster, and fragments of stones, as well, indeed, as in earth taken from a cultivated soil. Nay, it even flourished apparently equally

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* Mémoires de l'Acad. des Sciences, 1772, p. 229.

well in sand alone, in fragments of stone, in old plaster or mortar. An excess of argil or clay appeared to be prejudicial, principally by communicating the property of hardening after being moistened, so that water was not easily diffused through it, and the roots of the vegetable met with too great resistance. The same effect, it has been found from other experiments, arises from an excess of lime, especially where there is little vegetable or animal matter. In Tillet's experiments, no great advantage was derived from the addition of marl, and less benefit accrued from the mixture of vegetable and animal manure than might have been expected, from the advantage obviously derived from it in the practice of agriculture. He was disposed to conclude, from the results of all his experiments, that water is the most essential agent in promoting vegetation, and that the principal advantage of a soil is to preserve a certain degree of humidity, while it allows the roots to extend freely, and absorb it.

The following analysis of a fertile soil, in a climate in which much rain falls, that of Piedmont, is given on the authority of Giobert. One pound consisted of

Carbonaceous Matter	25 grains
Water	70
Silex from	4362 to 4475
Argil —	509 to 793
Lime —	283 to 679,

with a portion of air, about 19 grains, of which one third was carbonic acid, and the remainder carburetted hydrogen. In less fertile soils, the proportion of silex in the pound Troy was from 2716 grains to 4528, of argil from 396 to 1245, and of lime from 339 to 622. And in barren soils, the proportions were, of silex from 2368 to 4963, of argil from 1128 to 1692, and of lime from 225 to 620. In a drier climate, Bergman found a fertile soil to consist of four parts of clay, three of siliceous sand, two of calcareous earth, and one of magnesia. It appears, from the several analyses that have been made, that the less rain falls in a country, the proportion of calcareous earth in the soil must be increased, and that of siliceous earth diminished, to render it fertile. On this subject, some details are given in Kirwan's treatise *. Some facts have been also added by Davy, in a memoir on the analysis of soils †. The soils that are most productive of corn, he remarks, contain always certain proportions of argillaceous and calcareous earth, in a finely divided state, and a certain quantity of vegetable or animal matter. The quantity of calcareous earth is, however, very various, and in some cases very small. A very fertile corn soil from Ormiston in East Lothian, afforded in an hundred parts, only eleven of mild calcareous earth: it contained twenty-five parts of siliceous sand; the finely divided clay amounted to forty-five parts; it lost nine in decomposed animal and vegetable matter, and four in water, and afforded indications of a little phosphate of lime. Its fertility might be in some measure connected with this last substance, as it is found in wheat, oats, and barley, and may be a part of the food of the plant.

An important result, which appears to be established by some of Davy's analyses, is, that a soil may be fertile though it contain little vegetable or animal matter. A soil from the low lands of Somersetshire, celebrated for producing excellent crops of wheat and beans without manure, he found to consist of one-ninth of sand, chiefly siliceous, and eight-ninths of calcareous marl, tinged with iron, and containing only about five parts in the hundred of vegetable matter: no phosphate or sulphate of lime could be detected in it. And hence, as he remarks, "its fertility must have depended principally upon its power of attracting principles of vegetable nourishment from water and the atmosphere." This leads to an important inference with regard

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[*] Essay on Manures, p. 55. &c.

[†] Nicholson's Journal, vol. xii. p. 81.

to improving soils. "In supplying animal or vegetable manure, a temporary food only is provided for plants, which is in all cases exhausted by means of a certain number of crops: but, when a soil is rendered of the best possible constitution and texture with regard to its earthy parts, its fertility may be considered as permanently established. It becomes capable of attracting a very large portion of vegetable nourishment from the atmosphere, and of producing its crops with comparatively little labour and expence." Some alteration in its constitution, may, no doubt, arise from the mere succession of crops; but any deterioration from this cause may be obviated, by their judicious alternation, or by other methods which occasional analyses would suggest.

The results of analyses, considered as affording indications of fertility, must necessarily differ in different climates, and under different circumstances. "The power of soils to absorb moisture ought to be greater in warm and dry countries than in cold and moist ones, and the quantity of fine argillaceous earth they contain larger. Soils, likewise, that are situated on declivities, ought to be more absorbent than those in the same climate in plains, or in valleys. The productiveness of soils must likewise be influenced by the nature of the sub-soil, or the earthy and stony strata on which they rest. Thus, a sandy soil may sometimes owe its fertility to the power of the sub-soil to retain water; and an absorbent clayey soil may occasionally be prevented from being barren, in a moist climate, by the influence of a sub-stratum of sand or gravel."

From an extensive series of experiments on the analysis of soils (in which some new methods of analysis are introduced) by Professor Schubler, the general conclusion is established, that the qualities of soils, in respect to vegetation, are more dependent on their physical condition than on their chemical constitution, and that the physical properties may be very different, where the chemical constituents are the same *.

Besides a proper soil, the due application of heat and light are necessary, as has been already stated, to the process of vegetation,—heat, as a stimulus to excite and sustain the actions of the plants,—light, partly from the same operation, and partly from its chemical powers.

The particular statement of the circumstances influencing vegetation, presents the following general view of the series of chemical changes which constitute this process.

Regarding germination as its first stage, the seed exposed to humidity and atmospheric air expands: its farinaceous matter, by the action of the oxygen of the air, is converted into sugar, which serves as food to the infant plant. Its organs are gradually unfolded, and its nourishment is received from a different source: water, pure, or holding vegetable and animal matter in solution, is absorbed by the roots; and, in a soil containing decomposing vegetable and animal matter, different aërial fluids are received, and mingled with the sap. This, in its progress through the root, dissolves even part of the vegetable matter; and from this the plant, in the first stages of its growth, is better enabled to form its various parts. It is brought to the leaves of the vegetable, and is there presented, under an extensive surface, covered with a very thin membrane, to the action of the air and light: part of its water transpires; carbonic acid, and other elastic fluids from the atmosphere, as well as substances which these may hold dissolved, are perhaps absorbed; and, by the action of the vessels, assisted by the chemical agency of light, new combinations are established, and the proper juice of the plant is formed. This is conveyed by the footstalk of the leaf, and by vessels proceeding downwards through the bark, or between it and the wood: it is deposited in different parts, or is still farther

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* Annals of Philosophy, Vol. 7. 207. Vol. 8. 115.

changed in its progress,—changes from which the vegetable products are formed.

For the perfection of this process, the soil must be adapted to the nature of the vegetable; it must permit its roots to extend, allow access to the air, and convey and retain the necessary degree of humidity; its nutritive powers must in general be increased, by the intermixture of vegetable and animal matter; the decomposition of this must often be accelerated by other species of manure; and lastly, all the actions of the vegetable must be excited and sustained by the due proportion of heat and light.

From the substances conveyed to the plant from the air, water, and soil, must be derived the elements of which its products are formed. But in the uncertain state of our knowledge with regard to what principles are truly elementary, it is perhaps in vain to attempt to trace with certainty the source of those ultimate principles which the vegetable analysis affords. There are found in the products of the vegetable kingdom, though in very different proportions, oxygen, hydrogen, nitrogen, carbon, sulphur, phosphorus, the fixed alkalis, lime, magnesia, argil and silex, and several metals, particularly iron, manganese, and, as it has likewise been affirmed, gold. The origin of some of these is obvious; that of others is more obscure.

With regard to the oxygen and hydrogen, which constitute so large a part of vegetable matter, there is no difficulty; since they may be derived from the decomposition of the water which the plant absorbs, or a portion of the oxygen may be received from the atmospheric air.

Carbon is next to these the principal element of vegetable products, and in many of them is even contained in larger proportion; its origin is more doubtful. If carbonic acid be absorbed by vegetables from the air, and decomposed, it is evident that from this their carbon is acquired. But if plants, except when under exposure to solar light, consume oxygen, and give out carbonic acid, it is doubtful, whether the absorption of carbonic acid, if it do take place to any extent, exceeds the actual formation of it, much more whether from this absorption the progressive augmentation of carbon, which accompanies their growth, can be derived.

This difficulty exists even with regard to plants which grow in an ordinary situation, that is, in connection with the soil. When it is considered to how short a distance the roots extend in the soil, how little of this is carbonaceous matter, and how seldom, with regard to many plants, this soil requires to be renewed, it must be obvious, that the portion of carbon contained in it, or supplied to it by any natural process, cannot be equal to the quantity which in the progress of the growth of the vegetable is fixed in its composition; still less can it afford the larger quantity which the plant, except when under the influence of solar light, discharges under the form of carbonic acid.

The difficulty is greater where the plant grows when supplied merely with water and atmospheric air. Some have supposed, indeed, that in this case there is a mere expansion of the vegetable matter, and that the carbonaceous matter of the seed and root, affords the whole which enters into the composition of the grown plant. But independent of the quantity lost under the form of carbonic acid, the increase of matter is obviously such as to preclude this supposition. The fact has also been more rigorously demonstrated. An experiment made by Braconnot appears to be decisive. He inclosed in bottles, containing fine white sand, previously deprived of calcareous earth, by washing with weak muriatic acid, 460 seeds of white mustard. The sand was moistened with distilled water; the remainder of the bottle was filled with atmospheric air, freed from carbonic acid; and the bottles were closed accurately, and placed a few inches deep in a moist soil. Vegetation soon commenced; after six weeks growth, the plants were removed, washed with care, and dried.

They weighed 140 grains. Decomposed by heat they afforded 74 grains of coal; by incineration 51 grains of very alkaline ashes were obtained from this; and consequently it had contained 23 grains of pure charcoal. To afford a comparative result, 460 white mustard seeds were decomposed by heat, and only 62 grains of coal were obtained, which lost nearly half its weight by calcination. Hence it follows, as Braconnot remarks, that 460 mustard seeds acquired by vegetation in close vessels upwards of 15½ grains of pure carbon *.

Such facts add to the probability of the conclusion, that plants absorb carbonic acid from the atmosphere, and decompose it, retaining its carbon: otherwise no satisfactory account can be given of the origin of this element in vegetable matter.

The nitrogen, which, so far as our knowledge of the analysis of vegetable substances extends, enters in sparing quantity into their composition, may be derived from the atmosphere, or from the portion of it which water holds loosely dissolved, or from the soil.

Sulphur is contained in the roots and juices of some vegetables †, and, from the quantity of sulphates obtained by the incineration of plants, is perhaps a more common and abundant ingredient than has been usually supposed. Phosphorus enters into the composition of certain proximate principles contained in the nutritive grains and roots, and is yielded in the state of phosphate of potash and of lime, by the incineration of almost every variety of vegetable matter, as T. Saussure has shewn. But with regard to both, little can be said with precision. They may be derived from the soil; at least it has not been determined by any accurate experiment, whether they are contained in sensible quantity in vegetables which have grown sup-

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[*] Nicholson's Journal, vol. xviii. p. 25.

[†] Journal de Physique, 1781, p. 241.

plied with air and water alone. Braconnot has observed that radishes, which had been raised from seeds planted in well-washed sand, and supplied with pure rain-water, afforded traces of sulphur in their analysis; but the experiment can scarcely be regarded as sufficiently accurate, nor as precluding the supposition, that the small portion of sulphur might have been contained in the seeds.

The saline substances afforded by the vegetable analysis are various, and often in considerable quantity. Their bases are usually the fixed alkalis, and lime and magnesia; the acids with which these are combined are the sulphuric, muriatic, and carbonic, and, in more sparing quantity, the phosphoric. Silex sometimes exists as a deposite in certain parts of plants, particularly in the stems, and is generally contained in the matter which remains after the incineration of any vegetable. This residual matter, too, almost always contains iron, with which manganese is often associated.

It is not easy to determine in what state these substances exist in the vegetable. The salts may exist in it in the state in which they are obtained, or they may be formed during the incineration by the combination of their elements. It is not improbable, that even the alkalis and earths may have this origin, their bases existing perhaps as primary ingredients of the vegetable products. Whichever of these opinions be adopted, it is obvious that they may either be formed by the process of vegetation, or they may be derived by absorption from the soil, either in their primary state, or in the state in which they are obtained. The former conclusion has been inferred from the fact, that so many vegetables grow when supplied with air and water alone; while in opposition to it, it has been urged, that water is scarcely ever perfectly free from foreign matter, and that from this, or from the materials supporting the growing vegetable, these principles might derive their origin. It is difficult to obtain any earthy substance free from all saline and metallic matter; even water which has once been distilled may contain minute portions of these, and the atmosphere holds various substances in a state of mechanical suspension. Hence the difficulty of making such experiments, so that the result may be unexceptionable. And in plants growing in the soil, there is an abundant source of such principles. Some facts too, which have been long known, prove the connection of the saline matter in vegetables with the soil. Thus, marine plants usually contain muriate of soda, which diminishes in quantity, and at length disappears when they are transplanted to an inland situation: and certain plants which contain nitre, as pellitory, borrage, and others, do not flourish but in a soil containing nitrous salts.

The researches of Saussure on the analysis of vegetables, the results of their incineration, and the connection of these with the soil, have been extensive, with the view of elucidating this subject.

He established, in the first place, that analysis discovers all these substances in vegetable mould[*]; and farther, that they exist in solution in water which has macerated on that mould[†]. He also found, that plants absorb small quantities of saline substances, when these are presented to their roots in solution in water[‡], the quantity absorbed being greater with regard to some salts than with regard to others. Since these substances, therefore, are usually contained in the soil, and since they are capable of passing by absorption into the vegetable system, their presence in vegetables is rather to be expected, and it would even be surprising if they were entirely wanting.

Saussure farther found, by comparative trials on plants supplied with pure water, and with water in which certain salts were dissolved, that the saline matter which had been absorbed remained in the plant, and might be detected in the ashes formed by its combustion *. It likewise followed, from other comparative experiments, that when beans were made to vegetate, by being supplied in one arrangement with distilled water, being planted in another in gravel in glass capsules placed in the open fields, and supplied with rain-water, and in a third, being planted in the common soil in pots,—in all these cases, the quantity of ashes they afforded on burning was different; from 100 parts of the dried vegetable matter of the first, 3.9 parts of ashes were obtained; from 100 of the second, 7.5 parts; and from 100 of the third, 12 parts †; thus proving that a considerable portion of saline and earthy matter was conveyed from the soil.

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[*] Recherches, p. 280.

[†] Ibid. p. 292.

[‡] Ibid. p. 251.

In the last place, the proportions of the elements of the ashes have almost always a certain relation to the soil. Plants which have vegetated in a soil that has originated from the disintegration of a siliceous rock, furnish, other circumstances being alike, ashes which contain less lime and more silex than those which have grown in a calcareous soil. If the soil, however, contain much vegetable mould, this may not happen: the ashes will then be alike. This was established by an experiment made by Lampadius. He prepared in a garden five spots of four feet square surface, and one foot depth; in each he put a mixture of a pure earth, and of eight pounds of animal manure. He sowed rye-seeds in each; and the ashes of the plants produced were all found to contain the same principles. Lampadius concluded from this, that the earths found in vegetables are formed in vegetation; but, as Saussure has remarked, the manure, not having been analysed, might contain a sufficient quantity of those earthy and

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* Recherches, p. 259.

† Ibid. p. 281.

saline substances most congenial to the plant, and which it would absorb *.

All these facts appear in favour of the conclusion, that the saline, earthy, and metallic substances found in plants are derived from the soil.

From this conclusion, Saussure explained a number of facts connected with the production of ashes by incineration from vegetables, which otherwise have not been accounted for †. Thus, herbaceous plants afford more saline matter than those which are larger, and have more wood. Now, according to his experiments, saline matter is conveyed into the plant only by absorption of water holding it in solution, and this only in very minute quantity. It follows, therefore, that those plants which absorb and transpire most should contain the largest quantity of saline matter, as the largest quantity must be conveyed into their substance. But it is proved, by the experiments of Hales and Bonnet, that herbaceous plants transpire more than those of a larger size.

It may be expected, that the saline matter will be principally deposited in those organs in which transpiration is performed. These are chiefly the leaves; and accordingly, experiment has proved, that in a given weight, the leaves yield more saline matter than any other part of the plant. The bark, Saussure found, contains more than the interior parts, and obviously from a similar cause.

When the parts of a vegetable, the leaves for example, are washed repeatedly with water, they afford a smaller quantity of ashes on burning, than when burnt without this previous washing; which proves, that part at least of the saline matter obtained by their incineration, exists as such in the plant.

It is to be added to this general statement, that although these principles are chiefly derived from the soil, Saussure

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* Recherches, p. 283.

† Ibid. p. 274. &c.

found reason to conclude, from some experiments, that the atmosphere may afford a portion of them. The experiment by which this was to be determined was, obviously, to cause grains to grow in distilled water, and, by a comparative experiment, to determine whether the plants produced afforded more saline or earthy matter than was contained in the seed. On making the experiment, it was found, that there was a small increase of this matter during the vegetation, which, according to the views of Saussure, had probably been deposited from the atmosphere on the leaves of the plant *. This serves to explain the results of some experiments by Schrader, in which a portion of earthy matter, exceeding what was originally contained in the seeds, was obtained from wheat, rye, and other similar plants, which had grown in sulphur, (a substance which, of any that could be employed, was found to be most easily freed completely of any earthy matter), and been supplied only with distilled water; as in these experiments the atmospheric air was freely admitted.

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* Recherches, p. 304.

CHAP. II.

OF THE PROXIMATE PRINCIPLES OF VEGETABLES.

If the chemist, in the examination of the products of the vegetable kingdom, were under the necessity of investigating the properties and composition of the individual substances produced by every plant, the task, from its extent, could scarcely be executed. It is one, however, which is unnecessary; for however diversified the products of vegetation appear to be, they are all reducible to a few species, distinguished by appropriate characters. These form what are named the Proximate Principles of Plants; they are obtained by a very simple analysis, and are all compounds formed by the combination of the ultimate elements of vegetable matter.

Thus, suppose that the object is to discover the composition of the bark of any vegetable, it is not resolved at once into its ultimate elements; we first endeavour to discover of what immediate principles it is composed. If, with this view, it be subjected to maceration in water, it will probably communicate to the water colour, taste, and other sensible qualities. If it be heated with water in close vessels, a portion distils over, from which an oil may separate, possessing odour and taste. If it be digested in alkohol, a substance may probably be extracted, which had resisted the action of the water; and after repeated experiments of this kind, nothing is left, but the inert ligneous fibre. If it be inquired, what was the composition of the bark, the analysis warrants the conclusion, that it consisted of a peculiar matter soluble in water; of another, not soluble to any extent, but volatile at the temperature of 212; and of a third substance, neither soluble in water nor volatile, but capable of being dissolved by alkohol; these being attached to the ligneous fibre. In a similar manner, the seed or fruit of a vegetable, or any of its productions, may be analysed.

The result of such researches is the discovery of a certain number of principles, capable of being distinguished from each other by peculiar properties, and forming by their mixture or combination, all the varieties of vegetable matter. It is to these chiefly that the attention of the chemist is confined. It would not only be an endless task to examine chemically every individual vegetable substance, but it would be one, in a chemical point of view, comparatively without utility, since many would be found so much alike, that no discrimination of them as chemical agents could be established. Differences of sensible qualities exist, which are with propriety observed by the naturalist, or by the physician, as they are often adapted to important purposes in medicine or in the arts; but which are neglected by the chemist. They probably depend, indeed, on variations in the composition of the different substances; but such variations are too subtle to be traced with accuracy by chemical analysis. Thus, vegetable essential oils possess the same chemical qualities, and would afford, on decomposition, the same ultimate principles in the same proportions; or, if any difference were observed, it could never be clearly established, that this was the cause of the differences in their properties. And the case would be the same with regard to the other proximate principles. This necessarily leads to a more general examination, and the chemist must rest satisfied with reducing all these varieties to a few well-defined species; those under each species agreeing in their essential chemical properties and relations, though they may vary in their sensible qualities.

The first step, then, in the consideration of the vegetable substances, is the discrimination of these species, or of what are named the vegetable Proximate Principles. These exist in the entire plant in various states. Some are collected in particular organs, nearly pure; others are mixed with the common sap, or with each other; and some are chemically combined. Different methods, therefore, are employed to obtain them separate. Sometimes they are procured by spontaneous exudation; some may be obtained by mechanical expression; those which are volatile are separated by heat, and others are extracted by water, alkohol, or other solvents. When obtained separate, the requisite discriminations between them are established.

In the last place, it is necessary to investigate the composition of these substances. This is, however, extremely difficult: it is liable to all the inaccuracies arising from a complicated analysis; and we are unable to bring our conclusions to the surer test which synthesis affords.

The mode of effecting this analysis, which has been generally employed, is the application of heat. When a vegetable is raised to a temperature superior to 212°, in close vessels, the water it contains is first expelled: its decomposition then commences, and its elements enter into new combinations: a coloured empyreumatic oil distils over; this is followed by an acid which condenses in the fluid form: a quantity of aërial fluid is extricated, which is, in general, a mixture of carburetted hydrogen, carbonic oxide, and carbonic acid; and a quantity of charcoal remains, with minute portions of salts, earths, and metals. The nature of this analysis is sufficiently evident. The vegetable matter does not consist of all these products, but by the heat applied, the balance of attractions between its elements has been broken; these enter into new combinations, and form the oil, the acid, and other substances which the analysis affords. The oil is formed by the union of part of the hydrogen with part of the carbon of the vegetable matter; the acid, by the combination of another portion of carbon and hydrogen with oxygen; and the carburetted hydrogen, and carbonic acid, are products of the same principles, united in other proportions.

This analysis of vegetables by fire was often performed by the older chemists. They supposed, that by means of it they might discover the source of the peculiar properties of different kinds of vegetable matter. With this view, above one thousand different plants were analysed by the members of the French Academy, in the beginning of the last century, but with no advantage: the same products were afforded by the analysis of all of them; and these products not being such as pre-existed in the matter analysed, but originating from new combinations of its principles, could give no just idea of its composition, at a time when these ultimate principles were unknown.

Even modern chemistry derives limited information from such an analysis; at least without farther experimental investigation. Some general conclusions may indeed be drawn. If the substance analysed yields a large quantity of acid, we conclude, that it has contained a considerable quantity of oxygen. If it afford much oil, we conclude that it contains a considerable quantity of hydrogen, since this element is the principal constituent part of empyreumatic oil. When ammonia or prussic acid is afforded, we infer that the substance operated on contains nitrogen, as that element is necessary to the formation of either of these substances. In the same manner are discovered the earths and metals which the vegetable may contain; and from the quantity of charcoal which remains, some conclusion may be drawn as to the quantity of carbon. But to determine the composition with sufficient precision, farther experimental investigations are required: the acid, the oil, and the compound gases which have been procured, must be analysed, and the proportions of their elements ascertained. The process is thus rendered laborious and complicated; and the whole is still liable to the source of error arising from the uncertainty what proportion of the products of the analysis, of the water in particular, pre-existed in the vegetable matter, or has been actually formed.

Sometimes the proximate principles of vegetables are analysed by exposing them to heat, with the access of atmospheric air, and collecting the products of their combustion. From the nature of these we ascertain the nature of the elementary principles: and from the quantities, the proportions in which they were united. Oil, when subjected to this analysis, yields carbonic acid and water, and must therefore consist of carbon and hydrogen, either with or without oxygen. The quantity of carbonic acid produced, gives the quantity of carbon; the quantity of water the proportion of hydrogen; and by comparing the quantities of these products with the quantity of oxygen consumed, we discover whether oxygen has been an element in the substance analysed, and in what proportion. This method, when it is applicable, gives more direct results.

The proximate principles of vegetables are sometimes analysed by spontaneous decomposition. It is thus that sugar is brought into the state of fermentation; and from the products of the fermentation, the principles of the saccharine matter are determined. The analysis of these substances is in a few cases, too, effected by the agency of the acids, particularly the nitric, which communicate to them oxygen; and by the product the nature of their acidifiable base is ascertained.

A peculiar mode of analysing vegetable subtances has been introduced by Gay Lussac and Thenard. It consists in converting the vegetable matter, by oxygenation, into water and carbonic acid, by burning it by means of hyper-oxymuriate of potash, a substance which affords oxygen with so much facility, that the method has the advantage of being applicable to almost every variety of vegetable matter, while it affords also the most direct results. A certain weight of the body to be analysed is intimately mixed with fused hyper-oxymuriate of potash, both having been dried at the heat of boiling water, and the proportion of hyper-oxymuriate being used, which may be found by preliminary trials necessary to render the combustion complete. The mixture is made into small balls with water, and these are brought to dryness by exposure to the heat of boiling water. They are introduced successively into the apparatus by a tube with a stop-cock, having a cavity into which they are received, and to which heat is applied to excite the combustion. The quantity of oxygen which is furnished by a given weight of oxy-muriate of potash is known. To discover the products, the elastic fluid produced in the operation is collected over mercury, —the quantity of carbonic acid it contains is estimated by absorption by solution of potash; an excess of oxygen generally disengaged from the decomposition of the salt, will be found in the residual gas; any nitrogen gas mixed with it will be discovered by the removal of the oxygen by a eudiometrical process; and if any carburetted or oxy-carburetted hydrogen has been disengaged, it may be discovered by exploding the gas containing the excess of oxygen, with a given quantity of pure hydrogen gas. This will be consumed, any carburetted hydrogen gas present will likewise burn during the detonation; and the diminution of volume after the combustion will shew its quantity. Thus are obtained all the facts whence the proportions may be determined,—the quantity of oxygen consumed, the quantity of carbonic acid formed, which gives the quantity of carbon, and by comparison with the weight of the substance analysed, gives also the quantity of water produced, account being taken of any nitrogen evolved, or any carburetted hydrogen formed; and, lastly, if any fixed substance is afforded, it remains mixed with the residual muriate of potash, and its nature and quantity may be determined. Or this may be done by the incineration of the vegetable matter *.

This method is probably superior to any that had been before employed. It is liable however to some difficulties, particularly in determining with precision what quantity of water has pre-existed in the substance; this is more particularly the case in assigning the composition of the vegetable acids, as I shall afterwards have to notice, though the difficulty, it is to be acknowledged, is one connected with the vegetable analysis itself, rather than with the peculiar method employed. There must, however, in the process of these chemists, be an additional source of error from the mixture being moistened, and the uncertainty of its being brought again precisely to the same degree of dryness. Berzelius has remarked, too, that the quantity of hydrogen is determined from the loss of weight attending the operation, which in some cases may be owing, in part at least, to other causes; and as the equivalent combining quantity of hydrogen is so small, a very trivial error in its estimation leads to very important results †.

Some general conclusions were stated by Gay Lussac and Thenard, from the results of their experiments. They inferred, that in a number of vegetable substances, the proportions of the oxygen and hydrogen are those that form water, to which is added a certain proportion of carbon; so that this proportion of carbon, with a certain weight of water, would give the proportions of the elements of these substances. There are others in which the oxygen is present in a larger proportion to the hydrogen, than that which forms water; and in a third class there is an excess of hydrogen. From these facts they farther inferred, 1*st*, " That a vegetable substance is acid, when the oxygen in it is to the hydrogen in a larger proportion than that in water." *2dly*, "It is resinous or oily, when the oxygen in it is to the hydrogen in a smaller proportion than that which forms water. And, *3dly*, "It is neither acid nor resinous, when the oxygen and hydrogen are in the same proportion as that constituting water:" sugar, gum, starch, and the ligneous fibre, are the principal substances of this class. The following table gives the results by this method, and according to these views*.

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* Recherches Physico-Chimiques, tom. ii. p. 321.

† Annals of Philosophy, vol. iv. p. 402.

Substance analysed.	Carbon contained in that substance.	Oxygen contained in that substance.	Hydrogen contained in that substance.	Supposing the oxygen and hydrogen in the state of water in the substance.		
				Carbon.	Water.	Oxygen in excess.
Sugar	42.47	50.63	6.90	42.47	57.53	0
Gum-arabic . .	42.23	50.84	6.93	42.23	57.77	0
Fecula	43.55	49.68	6.77	43.55	56.45	0
Sugar of milk .	38.825	53.834	7.341	38.825	61.175	0
Oak-wood . .	52.53	41.78	5.69	52.53	47.47	0
Beech-wood .	51.45	42.73	5.82	51.45	48.55	0
Mucous acid .	33.69	62.67	3.62	33.69	30.16	36.15
Oxalic acid . .	26.57	70.69	2.74	26.57	22.87	50.56
Tartaric acid .	24.05	69.32	6.63	24.05	55.24	20.71
Citric acid . .	33.81	59.86	6.33	33.81	52.75	13.44
Acetic acid . .	50.22	44.15	5.63	50.22	46.91	2.87
						Hydrog. in excess.
Resin, common	75.94	13.34	10.72	75.94	15.16	8.90
Copal	76.81	10.61	12.58	76.81	12.05	11.14
Wax	81.79	5.54	12.67	81.79	6.30	11.91
Olive oil . . .	77.21	9.43	13.36	77.21	10.71	12.08

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* Gay Lussac has since said (Annals of Philosophy, vol. vi. p. 194.) that he considers these general conclusions as liable to exception. And Berzelius had before stated some results at variance with them, (Annals, vol. v. p. 178. vol. vi. p. 451.). The whole subject indeed, I shall immediately have to remark, is to be considered under a very different point of view.

Berzelius has submitted a number of vegetable substances to analysis, by a method somewhat similar to that of Gay Lussac; burning them in a tube with oxymuriate of potash, with the addition of a portion of fused muriate of soda to moderate the combustion, and with several minute precautions to insure accuracy *. The following table presents the results †:

Substances.	Oxygen.	Carbon.	Hydrogen.
Citric acid	54.831	41.369	3.800
Tartaric acid	60.213	35.980	3.807
Oxalic acid	66.534	33.222	0.244
Succinic acid	47.888	47.600	4.512
Acetic acid	46.82	46.83	6.35
Gallic acid	38.36	56.64	5.00
Saclactic acid	61.465	33.430	5.105
Benzoic acid	20.43	74.41	5.16
Tannin (from nutgalls) . . .	44.654	51.160	4.186
Common sugar	51.47	41.48	7.05
Sugar of milk	53.359	39.474	7.167
Gum-arabic	51.306	41.906	6.788
Potatoe starch	49.455	43.481	7.064

Some of these results correspond very nearly with those of Gay Lussac, others differ considerably. The coincidence in the examples of sugar of milk, gum, and starch, is as close nearly as is to be looked for even in a repetition of experiments by the same method. The discrepancies are principally in the vegetable acids. But here the difference is more apparent than real. In the experiments of Gay Lussac, these acids,—the oxalic, tartaric, citric, &c. were submitted to experiment, freed from any adhering water, by being dried at a temperature of 212°, or rather combined with a base such as lime, by which no water of composition is abstracted. But Berzelius, in conformity to the opinion, that the more powerful acids contain com-

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* Annals of Philosophy, vol. iv. p. 404. vol. v. p. 95. &c.

† Ibid. vol. vii. p. 45.

bined water, and that the composition of the real acid abstracted from this water is that which is to be determined, conducted the analysis in such a manner as to attain this. He combined the acid to be operated on with oxide of lead; the portion of combined water, as he considered it, was thus separated; the real acid remained in combination with the oxide of lead, and in this state it was submitted to the analytic process with the oxymuriate of potash. The results, therefore, must differ from those of the opposite method, in the abstraction of the oxygen and hydrogen of this water. But if the quantities of these are taken into account, it will be found that there is in general a very near coincidence with those of Gay Lussac, as I have shewn in a Memoir in which this subject is investigated *, and as will be more fully stated under the history of the vegetable acids. There is no just reason to admit the existence of this combined water; what is abstracted is the product of partial decomposition of the acid, conformable to what has been already explained in considering the theory of acids. And the proportions assigned by Gay Lussac, or those of Berzelius corrected by restoring these quantities of oxygen and hydrogen, are to be considered as correct. From the coincidence between them, they appear to be determined with more accuracy even than might be expected.

The composition of the following vegetable principles has been assigned by Th. Saussure †:

Substances.	Oxygen.	Carbon.	Hydrogen.	Azote.
Starch of wheat . . .	48.31	45.39	5.90	0.4
Starch sugar	55.87	37.29	6.84	—
Sugar of grapes . . .	56.51	36.71	6.78	—
Manna	45.80	47.82	6.06	0.32
Gum-arabic	48.26	45.84	5.46	0.44

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* Transactions of the Royal Society of Edinburgh, vol. viii. part 2.

† Annals of Philosophy, vol. vii. p. 46.

The results of the vegetable analysis are not easily brought under the law of definite proportions. In inorganic compounds, the constituent elements are generally in binary combinations; and where different compounds are found formed of the same elements, this is to so limited an extent, and the proportions are so different, and so well defined, that the difference of composition, and of course the peculiarity of constitution, can be determined with perfect precision. In the immense diversity of the vegetable compounds, on the other hand, there may be said to exist, with a few exceptions, only three elements, carbon, hydrogen, and oxygen; the diversity of proportions, therefore, giving rise to the different specific compounds is so great, while the differences are so minute, as scarcely to admit of any precise determination. In inorganic compounds, the few simple multiples in which the elements unite are easily observed, and the composition can in general be shewn by analysis to be conformable to these. But in vegetable compounds it seems impossible to trace them, the number of combinations from the same elements, and the diversities of proportions, being so great, as to be incapable of being reduced under the few multiples in which, from the other series of combinations, these elements appear to combine.

To obviate this, it might be, and indeed has been supposed, that these substances are sur-compounds,—that the elements combine two and two in some of the usual definite proportions, that these compounds again unite in other definite proportions, and that this kind of sur-composition may take place to a great extent. But there is nothing to sanction this hypothesis; it is not capable of being applied with the least degree of precision to the constitution of the vegetable compounds; nor can it be conceived that any possible combinations of water, carbonic oxide and acid, carburetted and super-carburetted hydrogen, with carbon, hydrogen, and oxygen, according to the few definite proportions that are admitted, should form all the diversities of vegetable matter.

Berzelius, in a disquisition on this subject *, has represented the chemical constitution of organic, compared with that of inorganic compounds, under another point of view. In the latter, one of the elements is to be considered as unity, with which the others combine in their first or lowest combining quantity, or in simple multiples of this;—that is, according to the atomic hypothesis, one atom of one body combines with 1, or with 2, 3, or 4 of another; or according to the hypothesis of volumes, adopted by this chemist, one volume of one body combines with 1, or with 2, 3, or 4 volumes of another. In organic compounds again, that is, in vegetable and animal substances, when three or more elements are in combination, a certain number of atoms or volumes of one of the elements are held to combine with a certain number of atoms or volumes of each of the other, without its following that any of them is necessarily to be considered as unity. And in general, accordingly, the combinations are those of 2 with 3, 4 or 5 of another, 3 with 4, &c. On this assumption, combinations in all diversity of proportions may be established. This view has been adopted by other chemists.

It amounts, however, to an entire sacrifice of the simplicity and uniformity of the system of chemical combination, and is the relinquishing indeed of its leading and most important principle. The views I have illustrated in different parts of the preceding volumes, of the relation of the constitution of some of the most important inorganic compounds, acids, and others, to the laws of definite proportions, lead to a solution of the difficulty, without departing from the principle, that in all combinations one of the bodies is to be regarded as a base, with which, considering it as unity, the others are combined. It has al-

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* Annals of Philosophy, vol. iv. p. 323.

ready been stated briefly, that this is the case in the composition of the vegetable acids, one of their elements, carbon, being the base, with which the others, oxygen and hydrogen, combine in definite proportions conformable to the usual law,—a result which will be illustrated more fully under their history. There is every reason from analogy to infer, that this will also hold true with regard to the composition of the other vegetable principles, other elements perhaps being the base. It has also been shewn in the illustrations of the same views, that there is every reason to conclude that the definite proportions in which the principal elementary bodies combine, are much more numerous than those which form merely the few specific binary compounds which can be obtained insulated. This being admitted, the diversities of composition in the vegetable (and likewise in the animal) products may be accounted for without the hypothesis of Berzelius, or without assuming any other principle than that which is applied to the more simple combinations of these elements in inorganic compounds. The whole series of chemical combinations will thus fall under the same law: and the progress of analysis in vegetable and animal chemistry, aided by the known laws of proportion, may at length determine the constitution of the specific compounds under these departments, with the same precision as that with which the combinations of inorganic matter are at present determined.

The Proximate Principles of Vegetables, that have been discriminated with precision, are Gum, Fecula, Jelly, Sugar, Gluten, Albumen, Caoutchouc, Wax, Fixed Oil, Volatile Oil, Camphor, Resin, Extract, Tannin, Indigo, Ulmin, Cinchonin, Emetin, Acids, Ligneous Fibre. To these are added, some that are more equivocal, as colouring matter, aroma, the bitter, acrid, and narcotic principles, and some others. Some principles, too, have been enumerated, the peculiarities of which seem to arise from intermixture, or from slight modifications of the others,—such as Inulin, Asparegin, &c. These may be noticed with the principles of which they appear to be varieties.

Of the preceding principles little uniformity is observed in distribution, in regard to the different parts of plants. The ligneous fibre forms the basis of the entire vegetable; the others are distributed through every part. Gum, fecula, saccharine matter, and oil either fixed or volatile, generally form the matter of the seeds; the acids are usually contained in the fruit; the extractive matter is generally diffused through the vegetable; tannin is found principally in the bark; the fixed oils are obtained either from the seeds or fruit, the volatile oils either from these, or from the wood, bark, or leaves. Gum, saccharine matter, and resin, often compose the secreted juices which spontaneously exude.

Scarcely any common chemical properties can be assigned to these principles, except the facility of decomposition which belongs to them, and the peculiar nature of their analysis from the re-action of their elements. With regard to other bodies, their relations are extremely different. Those of them which are acid, display this acidity in neutralizing the alkalis, earths, and metallic oxides. Those which are oily and resinous combine with the alkalis, and form soapy compounds, in which the alkaline properties are weakened to a certain extent. From the observations of Thenard * it appears, that several vegetable principles have the power of neutralizing acids; such are the essential and expressed oils. Tannin forms an intimate combination with acids; and it is doubtful if it has been obtained free from acid matter; and it is not improbable, he suggests, that a number of vegetable products may be compounds of the vegetable acids with other principles.

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* Memoires d'Arcueil, tom. ii. p. 5. 23.

SECT. I.—OF GUM OR MUCILAGE.

THIS principle of vegetable matter appears to be one of the first products of the changes to which the sap is subjected in the process of vegetation. It is contained in many plants; is found principally in the seeds and roots, but also in the stalks, bark, and leaves; and is sometimes formed in such quantity, as to be discharged by spontaneous exudation from the bark. It often exists in combination with some of the other proximate principles, particularly with fecula, sugar, extractive matter, and resin. There are seeds and roots, however, from which it can be extracted nearly pure, as from the seeds of the Linum usitatissimum, or the roots of Althæa officinalis. When discharged by spontaneous exudation, it is generally pure; and from some of the gums obtained in this manner, its characters as a distinct principle are derived.

This principle, when solid, forms Gum; when soft or liquid, Mucilage; in pharmacy, the latter term is applied to the watery solution of gum. Hermbstaedt introduced the distinction between gum and mucilage,—that gum forms with water a transparent glutinous solution, while mucilage forms a solution opaque and slippery: and they may, he adds, be separated from each other, by adding to their watery solution diluted sulphuric acid, which coagulates mucilage, without affecting gum *. This mode of separating mucilage from gum, Dr Bostock relates he never found to succeed. There are however some differences in the chemical properties of substances, which have been regarded as varieties of gum †, as Dr Bostock in his

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* Medical and Physical Journal, vol. i. p. 75. vol. iii. p. 370.

† Nicholson's Journal, vol. xviii. p. 36.

investigation of this subject has pointed out. The general character of the species may, therefore, be taken from a pure gum, as Gum-Arabic, and the peculiar properties of other varieties may then be noticed.

Gum is in fragments, smooth on the surface, semi-pellucid, with frequently a tinge of yellow or red: it is inodorous and insipid: it is neither fusible nor volatile: when heated, it softens and blackens, and is decomposed: it has little inflammability; for although, when heated in contact with the air, its carbon or hydrogen may combine with oxygen, it scarcely burns.

Gum is soluble in water, either cold or warm, in every proportion. Its solution is viscid, and, when the proportion of gum is considerable, is of a thick consistence, and is adhesive. By evaporation the gum may be obtained in a concrete form, and is soluble in water as before. Gum also absorbs water, which it retains in a solid state.

The solution of gum in water becomes sour on being kept for some time, from the formation of acetic acid. This change appears to arise from the re-action of its elements, and not from the absorption of oxygen. By no management can gum be made to undergo the vinous fermentation. When mixed with yeast, and kept in the proper temperature, it retains its natural taste, and acquires, after a number of days, only a peculiar offensive smell *.

Gum is insoluble in alkohol. This re-agent precipitates it from its watery solution, and this is the test by which gum is usually recognised. It is also insoluble in ether, and in oils, either volatile or fixed. From its viscosity, mucilage serves to diffuse oil through water, and to retain it in this state of diffusion, forming a milky mixture; for this purpose it is employed in pharmacy.

Gum is decomposed by the concentrated acids, the decomposition varying as to its products, according to the

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* Cruickshank in Rollo on Diabetes, p. 474.

kind of acid, and its concentration. Sulphuric acid blackens it, or evolves a quantity of its carbon: it causes also part of its oxygen and hydrogen to combine to form water; and a portion of acetic acid is produced.

Nitric acid exerts a different action upon it. No carbonaceous matter is separated; but the elements of the gum receive oxygen from the acid, and portions of oxalic acid, malic acid, and saccho-lactic acid, or mucous acid, are formed. The products however are different, according to the concentration or dilution of the nitric acid, and as its action is promoted or not by heat. Mr Cruickshank, by using a diluted acid, obtained from gum only oxalic acid. From treating an ounce of gum arabic with an equal proportion of nitric acid properly diluted, the quantity of crystals of oxalic acid formed amounted to 3 drachms 36 grains, and of oxalate of lime, formed by part of the acid combining with lime in the gum, about 6 grains; nor does any saccho-lactic acid appear to have been formed *. On the other hand, Fourcroy and Vauquelin found that the quantity of saccho-lactic acid, produced by the action of nitric acid on gum, is considerable, when the nitric acid is concentrated, and its action is promoted by heat; from 14 to 26 parts of saccho-lactic acid being obtained from 100 parts of gum. This saccho-lactic acid is contaminated with an intermixture of oxalate of lime, which may be abstracted by repeated digestions in very dilute nitric acid, which dissolves it. If the acid has not been boiled on the gum, or if it has not been concentrated or employed in too large quantity, malic acid is also formed with the oxalic acid, and it is converted into this latter acid, by the continued action of the nitric acid. From 100 parts of gum arabic, these chemists obtained 24 of malic acid †.

Oxymuriatic acid, applied to gum by a current of oxy-

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* Rollo on Diabetes, p. 468.

† Fourcroy's System of Chemistry, vol. vii. p. 197. &c.

muriatic gas being transmitted through a solution of it in water, converts it, according to Vauquelin, almost entirely into citric acid *. Muriatic acid exerts little action on it: the gum may be dissolved in the concentrated acid; the liquid becomes brown; a little carbon is separated; the gum is changed in its properties, but is not converted into any acid.

The alkalis and alkaline earths, when dissolved in water, dissolve gum without producing on it much change. Some salts produce effects of some importance, as affording characters by which this principle may be distinguished. The super-acetate of lead has no sensible effect on its solution, while the neutral acetate, or Goulard's Extract, gives a copious dense white precipitate,—Gummate of lead, as it is called by Berzelius, which he states to be composed of gum 61.75, oxide of lead 38.23. Nitro-muriate of tin does not precipitate gum. Solution of red sulphate of iron converts its solution into a transparent orange-coloured jelly. A solution of silicated potash renders it opaque, and at length a precipitate is thrown down, forming a test of some delicacy †.

From the decomposition of gum by heat we discover its elements and their proportions. The principal product is an acid liquid, which, as being obtained from the decomposition of mucilage by fire, has been named Pyro-mucous acid, and which appears to be acetic acid, with a little empyreumatic oil. With this an empyreumatic oil distils over; carbonic acid gas and carburetted hydrogen gas are produced, and there is a residuum of charcoal. From this analysis the composition, was inferred by Fourcroy and Vauquelin, to be 23.08 of carbon, 11.54 of hydrogen, and 65.38 of oxygen. The proportions assigned by Gay Lussac and Thenard, from the results of the more accurate analysis by

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* Annales de Chimie, tom. vi. p. 178.

† Bostock, Nicholson's Journal, vol. xviii. p. 28.

the oxymuriate of potash, are 42.23 of carbon, 50.84 of oxygen, and 6.93 of hydrogen. Berzelius gives as the proportions, carbon 41.752, oxygen 51.456, hydrogen 6.792*. And these differing little from those of Gay Lussac, are probably near approximations to accuracy. Those given by Saussure are considerably different, being carbon 45.84, oxygen 48.26, hydrogen 5.46, and nitrogen 0.44†. The presence of nitrogen in gum had been before indicated by Cruickshank. He observed, that when the acid obtained in its decomposition by heat is saturated with lime, a strong smell of ammonia is perceptible; hence this alkali had been formed in the decomposition of the gum, and of course nitrogen must enter into its composition. He farther found, that the residual charcoal contained lime, combined with phosphoric acid. From one ounce of gum arabic decomposed by heat, the residuum of charcoal amounted to 1 drachm 46 grains; when burnt, it left a whitish powder, amounting to about 10 grains, which was lime, mixed with a small portion of calcareous phosphate. Similar results were obtained from the substance named Gum tragacanth; one ounce of it yielded pyro-mucous acid, which, when supersaturated with lime, gave more ammonia than was disengaged from the acid obtained in the decomposition of gum arabic; the charcoal, when burnt, left a white residuum of 12 grains, which was lime, with a little calcareous phosphate. Lime was also discovered by re-agents in the solution of gum arabic in water: when a small quantity of sulphuric acid was added to it, needle-like crystals were slowly deposited; and when these were re-dissolved in distilled water, and oxalate of ammonia added, a copious precipitate of oxalate of lime took place‡.

Vauquelin found not only carbonate of lime, with a little phosphate of lime, in the ashes left after the combustion of gum, but likewise a small quantity of oxide of iron. The lime he supposes to exist in it, combined with an acid; as the solutions of gum, instead of giving indications of pure lime, indicate acidity; and gum, rubbed on paper moistened with a blue vegetable juice, rendered it red. The only soluble compounds of lime with a vegetable acid are those with the malic and the acetic. The former is only soluble with an excess of acid; it is probable, therefore, that it is with the acetic acid that it is combined,—a probability confirmed by the consideration, that acetic acid exists in the sap of vegetables of which gum appears to be one of the first products *. Berzelius considers the presence of both the nitrogen and lime as adventitious. The lime, however, appears to be essential, and to constitute an important difference between gum and other two principles with which it has some relations, fecula and sugar: they are capable of being made to pass into the vinous fermentation, which gum is not; and this difference appears to be owing principally to the presence of the lime, Cruickshank having found, that when lime is added to a solution of sugar, the latter is rendered incapable of the fermentative process †.

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* Annals of Philosophy, vol. v. p. 271.

† Ibid. vol. vii. p. 46.

‡ Rollo on Diabetes, p. 462. 465.

Gum is usually obtained by spontaneous exudation, or from incisions in the trunk and branches of trees. Its existence in vegetables is detected, by boiling the vegetable substance with water; the water dissolves the gum; and if much of it is present, the decoction is glutinous: when evaporated to the consistence of thin syrup, the addition of three parts of alkohol will precipitate the gum. The effects from the other tests already mentioned, also distinguish it.

Of the different gums, those obtained by spontaneous

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* Nicholson's Journal, vol. xii. p. 256.

† Rollo on Diabetes, p. 471.

exudation are the purest. Gum Arabic is the produce of the Mimosa nilotica, or, as the plant has been more lately named, Acacia vera, a native of Egypt and Arabia. It is white or yellowish, semi-transparent and brittle, insipid, and free of odour. It is soluble in water, forming a viscid solution. Gums exude from the cherry, plum, and other trees of this country, similar to gum arabic, but less pure, and more coloured. Dr Bostock has found, that the effects of re-agents on the cherry-tree gum are somewhat different. Acetate of lead does not throw down a precipitate from its mucilage, as it does from the other; there is only a slight tendency to coagulation, and the gum is separated from its solvent, in fine filaments. Nitro-muriate of tin converts it into a solid jelly; the solution of red sulphate of iron causes no precipitation nor coagulation in its solution; neither does alkohol precipitate it: a number of filaments are formed, but the greater part of the mucilage appears to incorporate with the alkohol. Dr John has given the name of Cerasin to a principle existing along with pure gum in the cherry-tree gum, the plum gum, and some others. It remains in the state of a soft glutinous mass, when they are treated with water; it is also insoluble in alkohol, but is dissolved in water acidulated with sulphuric acid, at a boiling temperature.

Tragacanth is the produce, by exudation, of the Astragalus tragacantha, or Astragalus verus. Though it is similar to gum, there are some properties in which it differs; and Hermbstaedt, from these differences, considered it as a variety of what he named Mucilage. It is not so easily soluble in water as gum. In cold water, it softens and swells without being dissolved. When boiled in water, it communicates to the liquor a great degree of viscidity; a very small quantity giving even the consistence of a jelly; but the solution remains turbid, with a number of filaments diffused through it. The effects of re-agents upon it are, according to Dr Bostock's experiments, different from those on gum arabic. Nitro-muriate of tin forms with its mucilage a firm coagulum; the solution of red sulphate of iron neither coagulates nor precipitates it; and it is not precipitated by silicated potash. According to Bucholz, it is a compound of jelly and gum.

The mucilages extracted by infusion from a number of seeds or roots, such as the linseed, quince seed, althæa-root, &c. have the general qualities of solution of gum, being thick and viscid, insipid, inodorous, and indefinitely soluble in water. Yet they exhibit some differences in the effects of re-agents. Mucilage of linseed is not precipitated by silicated potash, nor is it affected by red sulphate of iron, while super-acetate of lead and nitro-muriate of tin occasion in it considerable opacity. Alkohol precipitates slowly its solid matter in a fibrous form, without rendering the fluid opaque. The other mucilages appear not to differ much from this.

The differences which thus exist in different varieties of gum, do not appear to be very essential; it can scarcely be affirmed that they are constant, for the results are different in the experiments of different chemists; they probably frequently arise from intermixture; and even when they do not depend on this, they may arise from slight variations of composition, which cannot be regarded as sufficient to change the essential characters of the species. Cruickshank accordingly found, that gum arabic and tragacanth, which may be placed at the extremities of the series, as deviating most in their properties, are of the same composition; they afford, when decomposed, not only the products composed of carbon, hydrogen, and oxygen, but also the nitrogen and lime which are more peculiar to the constitution of gum.

From some of the vegetables of this country, gum or mucilage may be extracted in such quantity, that they afford a source whence an abundant supply may be derived for its consumption in some of the arts, particularly in calico-printing, in which it is largely used. Mr Willis observed, that the root of the plant called blue-bell or harebell (Hyacinthus non-scriptus) is extremely mucilaginous. A pound of the bulbs of this root, when dried, yielded about four ounces of a powder, which, by maceration in water, gives a strong mucilage, and, when employed for thickening the mordant and fixing the colours in calico-printing, was found to answer equally with gum arabic when used in the same proportion *. He afterwards discovered other vegetables, the roots of which afford a mucilage equally strong, particularly the vernal squill, (Scilla verna), and the white lily, (Lilium candidum), which might be used as substitutes for gum arabic †. Some experiments on the mucilage of the Hyacinthus non-scriptus, and on its application to useful purposes, have been likewise made by Leroux. He has given different methods of preparing it: that which answers best, is to macerate the bulbs of the root in a sufficient quantity of water to form a thick mucilage, which is expressed, and dried by exposure to the air. This mucilaginous matter appears, from his experiments, to have all the properties of gum ‡. Dr Bostock has remarked, that it contains a quantity of starch.

A discovery of still more importance is that of a method of extracting a mucilage, which may be employed as a substitute for gum, from the lichens which grow on the bark of our common trees and shrubs. The method was made public by Lord Dundonald ||. "The lichen does not consist entirely of a gummy matter. There is the outer skin or cuticle; below that a green resinous matter; the remainder of the plant consists of gum, a matter somewhat analogous to animal substances, and a small proportion of

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* Nicholson's Journal, 8vo, vol. vii. p. 30.

† Ibid. vol. ix. p. 234.

‡ Annales de Chimie, tom. xl. p. 145.

|| Philosophical Magazine, vol. x. p. 293.

fibrous matter, which cannot be dissolved by boiling, or the action of alkaline salts. The first process in preparing gum from it, is to remove the outer skin and the resinous matter. This is done by scalding the lichen two or three times with boiling water, allowing it to remain so long in the water as, by absorbing it, to swell: the skin cracks, and comes off with the greatest part of the resinous matter. Or it may be freed from them by gently boiling the lichen for fifteen or twenty minutes, then washing it in cold water, laying it afterwards upon a stone or brick floor, where it should lie for ten or twelve hours; the exposure for that time to air greatly facilitating the subsequent extraction of the gum. The scalded lichen is then to be put into a copper boiler with two wine gallons of water to every pound of lichen, and boiled during four or five hours, adding about half an ounce or three quarters of an ounce of soda or pearl-ashes for every pound of lichen; or, instead of these salts, about half an English pint of volatile alkali. The boiling should be continued until the liquor acquires a gummy consistence. It is then to be taken out, and allowed to drain through a wire or hair cloth. The residuum is to be put into a hair-cloth bag, and to be squeezed in a press. The first boiling does not extract the whole gum. The lichen should be boiled a second and even a third time, diminishing at each process the quantity of water and the quantity of alkali, which a little experience will soon point out. When three boilings are employed, the gummy extract of the last should be kept for the first boiling of the next lichen. The extract from the first and second boilings should be mixed together, and evaporated to the consistence necessary for block or press printing."

"When this mucilage is to be employed for making ink, manufacturing and staining paper, or for stiffening silks, crapes, and gauzes, it should be extracted from the lichen without employing any alkaline salts, continuing the boiling or digestion longer, and with a moderate degree of heat, in which case the gummy extract will be nearly colourless. When volatile alkali is used, the boiler should be of iron, as volatile alkali acts on copper." From a calculation which Lord Dundonald adds, it appears that the mucilage thus obtained may be used with much advantage as a substitute for gum; and it has been employed by the calico-printers of this country, in some of their processes. There is some reason to believe, that the substance thus extracted from lichen approaches nearer to the nature of fecula than of gum. It is highly nutritious; and Proust, in a memoir on its use as food, has remarked, that it is not soluble in cold water *.

Gum is not an active substance in its effects on the living system. In medicine, it is used for its lubricating quality; and so little activity does it exert, that it has been taken as an article of food. Though thus inactive, the virtues of many vegetables depend on a gummy matter.

From its chemical properties, gum is of rather more importance. As a component part of vegetable matter, it renders the other parts more soluble in watery liquors. In pharmacy, it is used as a medium to suspend oils, balsams, and resins, in water. In the arts, the different gums are applied to various purposes, from their adhesive quality, and to diffuse powders in watery fluids: they are thus used in dyeing, ink-making, calico-printing, &c.

SECT. II.—OF FECULA, OR STARCH.

THE term Fecula, or Starch, is appropriated to a proximate principle of vegetables, similar in many of its properties to gum. It is a dry, white, insipid powder, which

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* Nicholson's Journal, vol. xvi. p. 210.

forms the principal part of the nutritive grains and roots. It is extracted by beating them in water, or by working the powder of them, made into a paste with water, in the hand: the soluble parts are dissolved; the fibrous and glutinous parts remain; and there is diffused through the water a fine powder, which gradually subsides, and may be dried. This is termed the Fecula of the plant.

If wheat flour, for example, be made into a paste with water, inclosed in a bag, and pressed, while a stream of water is poured upon it, the greater part is carried off in the form of a white powder, which forms the substance named Starch. This is a pure fecula. A similar product may be obtained from rye, and, in general, all those grains which are used as food. It can also be obtained from the potatoe, and from other roots and stems of plants. Sometimes it is extracted from the most poisonous or acrid plants, the poisonous or acrid matter being soluble in the water, and being thus abstracted from the fecula.

The principal of these is the starch of wheat; it is prepared in the following manner: The grain, well cleansed, is kept in cold water until it soften and swell, so that the husk separates; by pressure, it then gives out a milky fluid. The grains are put into a hempen bag, and pressed or beat, cold water being poured on them in sufficient quantity. The fecula is thus diffused through the water. As the water receives from the grain at the same time a quantity of saccharine matter, it soon runs, in the temperature at which it is kept, into the acetous fermentation; and the weak acid thus formed, by digesting on the fecula, renders it whiter than it otherwise would be, apparently by dissolving part of the gluten of the wheat. After it has subsided, the clear liquor is run off; the precipitate is washed with water; the water is drained off, and the starch is dried in a stove *.

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* The process, as it is conducted in this country, is particularly described in Aikin's Chemical Dictionary, article STARCH; and in the 29th volume of the Philosophical Magazine.

When, by any process of this kind, a fecula is obtained pure, it forms a light white powder, very soft to the touch, and when surveyed in a strong light, appearing in minute brilliant grains: it is insipid, and inodorous. Sometimes it retains a portion of the other principles of the plant, from which it receives colour, smell, or taste.

The property by which this principle is distinguished, is its complete insolubility in cold water, while with hot water it forms a gelatinous solution. Its insolubility in cold water is shown in the mode in which it is prepared, as, although it is suspended in a state of very minute division, no portion is dissolved. It dissolves in hot water at a temperature of 160 or 180, and the solution is more or less gelatinous, according to the proportion of water. This jelly may be dried into a stiff hard mass, which is still insoluble in cold, soluble in hot water. This insolubility in cold water, while it is soluble in warm water, distinguishes fecula from gum, and characterizes it as a peculiar principle. Lagrange found, that by gentle roasting fecula becomes soluble in cold water, and is thus so far assimilated to mucilage or gum. Dobereiner has observed, that if starch is only roasted slightly, so as to be of a grey colour, it is dissolved, though not entirely, by successive portions of cold water; the solution is yellow, and insipid; by evaporation it forms a yellowish pellucid mass, which dissolves in cold water, and forms a viscuous liquor, which is rendered milky by alkohol. If the starch is more thoroughly roasted, so as to become brown, it becomes entirely soluble in cold water, and forms a solution less viscuous, but in other respects the same *.

Fecula is entirely insoluble in alkohol, or in ether.

The acids, when much diluted with water, dissolve fecula, especially if the temperature be raised, and form a gelatinous solution. If concentrated, they decompose it.

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* Annales de Chimie, tom. xc. p. 29.

Sulphuric acid blackens it, by evolving a portion of charcoal, and water and acetic acid are formed. In a certain degree of dilution, and by particular management, it converts it into a product analogous to sugar, as is to be stated under the history of that principle. Nitric acid dissolves it, and affording oxygen, converts it into malic and oxalic acids. This action takes place most completely when the nitric acid is a little diluted, and a moderate heat is applied. Muriatic acid dissolves it, producing a decomposition somewhat analogous to that by diluted sulphuric acid.

The alkalis, when in solution in water, dissolve fecula, or reduce it to the consistence of a jelly, without the assistance of heat. The acids separate it from this combination. Dr Bostock found, that the solution of starch is precipitated copiously by acetate of lead, the combination of the starch and oxide of lead being so complete, that the water of the solution remains limpid. Berzelius has stated the composition of this amylate of lead, as he calls it, at 72 of starch, and 28 of oxide of lead. Nitro-muriate of tin throws down an abundant precipitate from solution of fecula. Silicated potash causes no obvious change. Alkohol throws down a precipitate similar to that from solution of gum.

Iodine forms a peculiar combination with starch. When they are rubbed together dry, a blue colour is acquired. When dissolved in water, with a very slight addition of sulphuric acid, it has the same colour, and this so deep as to form the most delicate test of iodine. With an excess of starch the colour is reddish, or nearly white, but the addition of sulphuric acid produces the blue tint.

Fecula is converted into saccharine matter by the process of germination, the theory of which has been already considered, (page 35.). The product, however, is not altogether pure sugar, but differs in some of its properties. Dobereiner found, that, when extracted by infusion in water, it cannot be rendered concrete, but forms by evaporation a viscid mass; it is also less sweet; it is not soluble in highly rectified alkohol, but is even precipitated by it from its concentrated watery solution; it is dissolved by diluted alkohol, and by this means may be separated from the starch, mucilage, and gluten of the grain. This conversion of fecula into a saccharine product, is effected in the process of malting on the nutritive grains, as preliminary to vinous fermentation. The fecula when mixed with yeast, and infused in hot water, is directly susceptible of the same process, so that the liquor, by distillation, can be made to afford ardent spirit. If previously roasted, it does not suffer, according to Dobereiner, either of these changes, a farther proof of its approximation in that state to the nature of gum.

Fecula exposed to heat, blackens, swells, and forms a spongy charcoal. If strongly heated, with the admission of the air, it burns: in close vessels, it affords a large quantity of pyro-mucous acid, with a little empyreumatic oil; carbonic acid and carburetted hydrogen gases are extricated, and a portion of charcoal remains. From these products its elements are evidently carbon, hydrogen, and oxygen. Some traces of phosphate of lime are to be found in its ashes; but this may arise from the gluten often associated with fecula, a small portion of which may adhere to it. The proportions of its constituent principles, as found by Gay Lussac and Thenard, are 43.55 of carbon, 49.68 of oxygen, and 6.77 of hydrogen. Berzelius has stated the composition of potatoe starch at 43.48 carbon, 49.46 oxygen, and 7.06 hydrogen: and Saussure that of wheat starch at 45.39 carbon, 48.26 oxygen, and 5.90 hydrogen.

Fecula exists in large quantity in all the nutritive seeds and roots, generally mixed with other principles. It does not appear to be completely formed but in certain stages of vegetation. Thus, in the nutritive grains, it is perfect only when they have attained maturity: previous to that period, it is in a state approaching to mucilage mixed with saccharine matter. It is probably formed from mucilage in the progress of vegetation; and Leroux, in his experiments on the mucilage of some of the tuberose roots, observed, that, in the drying of the mucilage, a portion of it appeared to be converted into fecula *.

This principle is sometimes employed in its pure state medicinally, from its nutritious quality, and from being easy of digestion. Sago and salop are feculas of this kind. The former is the produce of the Cycas circinalis, and is extracted from the pith of the stem and branches, by maceration in water: it is washed, and passed through a perforated copper plate, to reduce it to grains, which are dried. Salop is the produce of the Orchis mascula. Arrow-root powder is the produce of the Maranta arundinacea. Cassava is pre-pared from the tuberose root of the manioc, (Jatropha manihot): with the fecula of this root, there is associated an acrid and poisonous juice, which is separated by washing, in the process by which it is extracted. The roots of the Bryonia alba and the Arum maculatum are likewise composed principally of fecula, with acrid matter, which is separated in the process by which the fecula is extracted from them. These were formerly prepared for medicinal use. Wheat affords perhaps a larger quantity of fecula than any other vegetable substance, and in a state of perfect purity. A very pure fecula, in large quantity, is also extracted from the potatoe, the root being peeled, well cleaned and rasped, the pulp being placed on a hair-sieve, and water poured on it until the fecula is extracted. When dried it amounts, according to Dr Pearson's experiments, to from 15 to 17 parts in 100 of the root; with this are 8 or 9 of fibrous matter, and 5 or 6 of mucilage †, the remainder is water. Mr Skrimshire obtained similar results: Lampadius from 100 parts obtained, in different varieties of the potatoe,

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* Annales de Chimie, tom. xl. p. 156.

† Repertory of Arts, vol. iii. p. 389.

from 12 to 18 of starch, from 5 to 8 of fibrous matter, 1 of albumen, and 1 of extractive matter, with from 70 to 75 of water *. Potatoe starch has been used as a substitute, in stiffening linen, and similar purposes, for the starch of wheat. Lastly, some of the lichens contain a large quantity of fecula; and the Lichen islandicus, which has been celebrated for its mild nutritive quality, consists entirely of it, so as to afford a fecula nearly pure, when reduced to powder. Proust has given some observations on the method of preparing it for food †.

Fecula is, of any variety of vegetable matter, best adapted to the nourishment of animals; and it forms the principal part of all the seeds and roots which are used as food by man. Its nutritious power is well shown, by the fact, that some of the most nutritive of these, as rice, or the potatoe root, contain no other principle that can contribute to this, but fecula. Thus, the root of the potatoe, according to Dr Pearson's analysis of it, contains, besides fecula, only a small portion of mucilage and fibrous matter; yet, as he remarks, "there is sufficient evidence, that the potatoe root and water, with common salt or other seasoning, can nourish as well as any other vegetable matter and water, with seasoning." Some observations on the nourishing quality of fecula, and on the forms under which it may be employed, have been made by Mr Skrimshire ‡.

Fecula, besides its use, either pure, or under the form of the nutritive grains as an article of diet, is used in the state of its gelatinous solution, for pasting, and stiffening linen or other kinds of cloth. It also enters into the composition of some pigments.

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* Annals of Philosophy, vol. v. p. 59.

† Nicholson's Journal, vol. xvi. p. 210.

‡ Ibid. vol. xxi. p. 182.

Rose pointed out a principle analogous to fecula, which is extracted from the root of elecampane, (Inula helenium). This has been named Inulin. It is deposited from the decoction of the root, after it has stood for some hours. It is insoluble in cold water, but is soluble in boiling water: the solution, though liquid while hot, becomes gelatinous as it cools; and in the course of some hours, the water deposites the greater part of the substance dissolved, in the form of a compact white powder. Alkohol precipitates it from its solution in water. This white matter, thrown on burning fuel, melts like sugar, and evaporates, diffusing a white pungent smoke, and leaving a small coally residuum. At a red heat, it burns with a white flame. By distillation, it gives an empyreumatic acid, without any empyreumatic oil. Nitric acid converts it into malic and oxalic acids, and, when in excess, into acetic acid. From these properties, Rose inferred, that this substance is neither gum nor fecula, but intermediate between them; and he considers it as probable, that several products, which have been regarded as varieties of fecula, are of the nature of this powder *. Some additional facts with regard to it, leading to the same conclusion, have been stated by Gualtier de Claubry. He finds that hot water dissolves four or five times its weight of it, but without forming a gelatinous solution; the liquor when concentrated is merely viscuous: the inulin deposited by cooling contains so much water, that it may be liquified by raising the temperature. Potash dissolves it, but does not render it gelatinous: concentrated sulphuric acid precipitates it from this solution. Sulphuric acid dissolves it, rendering it brown; the inulin is precipitated by ammonia; nitric acid dissolves it, and

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* Nicholson's Journal, vol. xii. p. 97.

when heated decomposes it; muriatic acid does not dissolve it, as it does starch. Barytes precipitates inulin from its watery solution, by combining with it; strontites and lime do not: silicated potash and metallic solutions do not affect it: infusion of galls precipitates it. It does not form with iodine the fine blue colour which starch does, but a compound of a greenish yellow colour *.

SECT. III.—OF JELLY.

THE juices of certain fruits, as the currant, when expressed, if not too watery, concrete into a kind of tremulous jelly. There is none of the known principles of vegetables to which this property can well be assigned: for fecula, though it gives a gelatinous consistence to hot water, is not soluble in cold water, and does not naturally exist in solution; it is therefore necessary to consider it as distinctive of a peculiar principle, to which the name of Jelly may be given. There is an animal matter which has received the name of gelatin, which has the property of forming, with water, a tremulous jelly; but, except in this particular, vegetable jelly has no similarity to it, nor does it even approach to animal matter in its chemical characters or composition: it is not liable to putrefaction, but suffers that slow decomposition which vegetable matter in a humid state usually undergoes. Scarcely any observations have been made on this principle, except what has been incidentally stated by Vauquelin in his analysis of vegetable substances, particularly in a memoir on the analysis of the fruit of the

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* Philosophical Magazine, vol. 46. p. 295.

Tamarind *, and in another on the analysis of the pulp of the Cassia fistula †, in both of which it is contained.

It is soluble only in small quantity in cold water, even with agitation; but boiling water dissolves it abundantly, and the solution forms a jelly when it cools. It is necessary, to obtain the gelatinous consistence, that there should be a certain proportion between the gelatinous matter and the water; and if boiled long with water, it loses the property of forming a jelly. Hence the reason, as Vauquelin has remarked, that in the preparation of the vegetable jellies, which are formed by boiling the juices of certain fruits with sugar, it often happens, that if the proportion of sugar is not sufficiently large to absorb the water of the juice, or form with it a syrup, and if, in consequence, it is necessary to boil the liquor to dissipate part of the water, it does not concrete into a jelly on cooling.

Jelly may be obtained solid by drying. That from the pulp of Tamarind, Vauquelin found to be transparent.

This principle unites easily with alkalis: nitric acid causes it to pass into oxalic acid, without disengaging from it any sensible proportion of nitrogen: it forms a precipitate with infusion of galls. When subjected to destructive distillation, along with the elastic fluids usually obtained from the decomposition of vegetable substances, it affords much pyro-mucous acid, very little oil, and almost no ammonia. When burnt, its ashes yield a little carbonate of potash, carbonate of lime, argil, and oxide of iron.

Fourcroy supposed that this gelatinous matter is a combination of mucilage and vegetable acid;—an opinion that is vague, and liable to the objection, that it is not obvious how the addition of the acid could so far modify the properties of mucilage, nor is there any proof that it produces such an effect.

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* Annales de Chimie, tom. v. p. 101.

† Ibid. tom. vi. p. 282.

SECT. IV.—OF SUGAR.

SACCHARINE matter is often mixed with fecula in the seeds and roots of vegetables. It exists in still larger quantity as one of the secreted or proper juices of the plant. It is not a constant principle, but is formed chiefly at certain periods of vegetation. In fruits it is found in abundance only in a state of maturity; and in those plants which afford it in largest quantity, it is more abundant at certain periods than at others.

The plant named the Sugar Cane (Arundo saccharifera) has long been cultivated for the production of sugar. The juice of it, at a certain season, consists principally of saccharine matter: it is pressed out by subjecting the canes, cut short, and tied in bundles, to the pressure of three upright iron rollers or cylinders, the middle one of which is made to revolve. The expressed juice is clarified, by heating it with a quantity of pure quicklime, by which the portion of acid present in the juice, and which prevents the concretion of the sugar, is neutralized; the lime in combination with this acid, and also with carbonic acid, and with a portion of vegetable or herbaceous matter, is precipitated: towards the end of the operation, a scum collects on the surface, consisting of the mucilaginous and oily matter of the juice, with any grosser impurities entangled in it. When this is fully formed, the fire is damped, and the liquid is left at rest, to become clear. It is afterwards run into the evaporating boiler, in which it is made to boil: it is removed from one evaporating vessel into another, as the evaporation proceeds, until it be so far boiled down, that on cooling, the sugar concretes. It is then run into the cooler, a large shallow wooden vessel, in which this operation takes place; and from the concrete sugar, the remaining liquid part, the Molasses, is drained off*.

The sugar thus obtained is in small crystalline grains, of a brown colour, and is not perfectly pure. It is sometimes obtained purer, by running the inspissated juice into conical vessels, the apex of the cone being undermost, in which it is allowed to concrete; by an aperture at the bottom, the remaining liquid is withdrawn, and there is applied at the top a layer of clay, which is kept moist with water: this water filtrates slowly through the sugar, and removes the molasses.

In Europe, the sugar is purified by a process somewhat similar. It is dissolved in lime-water, and boiled, the lime being supposed to neutralize a small portion of acid present in the unrefined sugar, and probably precipitating a little extract: a quantity of blood is added, which forms a coagulum during the boiling, that rises to the surface, and entangles the impurities. The clear liquor is boiled down: it is run, when cold, into conical clay moulds, which are placed with the apex of the cone undermost: when it has become concrete, an aperture is made at this point; the base of the cone is covered with clay, which is moistened with water; and this water, slowly transuding through the sugar, removes any superfluous syrup; the conical loaves are dried in a stove. This operation is sometimes repeated: the sugar is then brought to the state of greatest purity: it is in the form of a mass, composed of crystalline grains, white, and having a taste perfectly sweet, without any peculiar flavour †.

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* Several improvements were introduced into the process by Dr Higgins, which are described in the 24th volume of the Philosophical Magazine.

† An improved method of refining of sugar has been introduced by Mr Howard, in which, by a more perfect filtration, the treacle is more completely and economically abstracted, and the concen-

Other plants besides the sugar cane produce saccharine matter in great abundance. In America, large quantities are obtained from the sugar maple, (Acer saccharinum). According to the account given by Dr Rush, the saccharine juice is most abundant in the tree in the spring; the stem is bored at that season with an auger, in an ascending direction, and the aperture is deepened gradually to the extent of two inches. When the juice ceases to flow, a similar aperture is made in another part; and in the course of four or six weeks a large quantity is collected. The saccharine matter is procured by boiling the juice until the greater part of the water is dissipated; a small quantity of slacked lime being added, with a portion of milk, or of the white of eggs, to clarify it, and a little butter, to prevent the liquor from boiling over the vessel. The sugar is made to concrete, and is clayed and refined nearly in the same manner as is practised in the manufacture of sugar from the sugar cane. From the juice yielded by a tree of the usual size, five pounds of sugar may be extracted, and the operation can be repeated annually, the tree not being injured by the tapping *.

The beet (Beta vulgaris), the parsnip, (Pastinaca sativa), the carrot (Daucus carotta), the turnip (Brassica rappa), and other plants allied to these in their natural characters, contain, at certain periods of their growth, juices possessed of considerable sweetness; and Margraaf extracted from all of them a portion of sugar †. Some years ago, the production of sugar from the beet engaged the attention of the German chemists; and it was to a certain extent cul-

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tration of the filtered liquor is, by an abstraction of atmospheric pressure, effected at a lower temperature, so that the conversion of a portion of sugar into treacle, which takes place at a higher temperature, is prevented, (Thomson's Annals, vol. viii. p. 209.)

* Transactions of the American Phil. Society, v. iii. p. 64.

† Mémoires de l'Acad. des Sciences de Berlin, 1747.

tivated, to obtain a substitute for the sugar of the West-India islands. Different memoirs on this subject were published by Achard*, Hermbstaedt†, Lampadius‡, and others. The general process for extracting it, as described by Achard‖, consists in softening the roots, by boiling in water, cutting them in slices, and expressing the juice by a press. The expressed juice is strained, and is reduced by boiling to about two-thirds. It is then strained, and is reduced, by farther boiling, to about one-half. It is strained a third time, and is reduced to the consistence of a syrup. This syrup, put into shallow earthen vessels, is kept in an apartment heated by a stove to a temperature of from 80 to 120 of Fahrenheit, until the sugar is deposited in an irregular crystallized mass. The remaining liquid is poured off, and the mass of sugar is subjected to pressure to render it dry. The addition of a portion of lime-water in the boiling has been supposed to facilitate the concretion of the sugar, and it is useful, according to Lampadius, in neutralizing the acid contained in the juice. He recommends also the expressing the juice from the roots without previous boiling, adding in the boiling a portion of milk, which, by its coagulation, serves to clarify the juice; and reducing the heat in the last stage of the evaporation §. Achard, in a process which he gave subsequent to the first, employs a little sulphuric acid to coagulate the albumen of the juice, and afterwards lime, to abstract this acid, and promote the crystallization of the sugar ¶. Chaptal, who conducted the manufacture of beet sugar on a large scale in France, during the interruption of commerce, employed nearly the same process. On the

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[*] Nicholson's Journal, 4to, vol. iii. p. 257. 288. 474.

[†] Ibid. p. 333. 410.

[‡] Annales de Chimie, tom. xxxviii. p. 76.

[‖] Ibid. tom. xxxii. p. 264.

[§] Ibid. tom. xxxviii. p. 76.

[¶] Nicholson's Journal, vol. xii. p. 259.

supposition that it may, under particular circumstances, be had recourse to with advantage, he has given the whole details in an elaborate memoir *.

Hermbstaedt obtained, from 125 lbs. of the roots of the Beta vulgaris, 5⅓ lb. of brown sugar, and 1⅞ lb. of syrup, which drained off †. This sugar has rather a disagreeable taste, but by clarifying the juice with the white of an egg, (for which, in the large way, blood might be advantageously substituted), it is obtained white and pure ‡; it is usually in the state of a powder, but it can be crystallized, exactly in the same manner as the sugar of the sugar cane. The produce is much dependent, as Achard has shown, on the methods practised in the cultivation of the plant; and even in countries where labour is cheap, in Germany for example, it can scarcely be cultivated to the same advantage as the sugar cane is in the West Indies.

Sugar is also contained in large quantity in many fruits, —the grape, fig, apple, pear, &c. hence the great susceptibility of their juices to fermentation, and the vinous liquors they afford. In the grape it is so abundant, that it may be economically extracted from that fruit, as Proust has shown. The process consists in adding to the clear juice heated, as much of an alkaline ley as is necessary to neutralize any free acid. It is then boiled down to one-half, and left to cool, until the saline matter of sparing solubility separates. It is next clarified by being heated with blood; and is lastly boiled down to the consistence of a syrup. This, after ten or fifteen days, condenses into a yellow granular mass, which consists of a concrete sugar, equal to about three-fourths of the mass, a portion of fluid sugar or syrup, and a minute quantity of extractive matter, gum, and malate of lime. This concrete sugar as-

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* Annales de Chimie, tom. xcv.

† Nicholson's Journal, 8vo, vol. xiii. p. 267.

‡ Ibid. 4to, vol. iii. p. 168.

sumes a kind of granular crystallization, and may be reduced to a dry powder, but cannot be brought into an indurated form. Proust, as is immediately to be stated, has distinguished this grape sugar as a different species from the sugar of the sugar cane.

Sugar is also formed from fecula in the process of germination, and in this process artificially conducted in the operation of malting. During this change oxygen is absorbed, and carbonic acid is formed, as has been already explained. The product is more analogous to the sugar of the grape, than to that of the sugar cane.

Another process has been discovered within these few years, by which sugar is formed from fecula, by the agency of sulphuric acid. The discovery was made by Kirchoff, a Russian chemist. One hundred parts of starch, four hundred of water, and one part of sulphuric acid, are the proportions to be used. To one half of the water the acid is added, and it is brought to boil in a copper vessel well tinned; the starch is diffused through the other half of the water, and this is added gradually, in small portions at a time, to the acid liquor. The whole is kept boiling for thirty-six hours, adding water occasionally to supply the evaporation. Some charcoal is then added; and, lastly, as much chalk as is sufficient to neutralize the sulphuric acid. After a little additional boiling the liquor is strained, to separate the sulphate of lime: if the process has been properly performed, it is colourless and transparent: it is then evaporated to the consistence of syrup, and is set aside to crystallize, which it usually does in two or three days, affording a kind of granular mass, similar to the sugar of the grape. The process does not succeed with the flour of wheat, or of the potatoe; but the starch of the potatoe affords the product as well as, or even better than, wheat starch. The proportion of sulphuric acid may, according to Vogel, be increased with advantage to 2 parts; and the time of boiling may be shortened, by increasing the proportion: thus, if 5 parts of acid are added to 100 of starch, only six or eight hours boiling, according to Schrader, are required. According to Nasse, nitric and muriatic acids produce the change as well as sulphuric acid. The theory of the operation is not easily explained. Vogel and De la Rive have ascertained, that no elastic fluid is discharged; that the presence of the air is not necessary, and that the sulphuric acid is neither decomposed nor combined with the starch. It might be inferred, therefore, conformable to the action which this acid often exerts on vegetable substances, that it merely causes part of the oxygen and hydrogen of the starch to combine and form water, the remaining elements forming the saccharine product; and this opinion was proposed by Vogel. But it is not probable that this kind of action will be exerted when the acid is diluted with so much water. Th. Saussure, too, has stated from experiments, that the weight of the sugar exceeds a little that of the starch from which it has been produced. He concludes, therefore, that starch sugar is nothing more than a combination of starch with water in a solid state, and that the acid causes the change merely by promoting the fluidity of the aqueous solution, and thereby facilitating its combination with the starch. But this explanation is not more satisfactory, since starch dissolved at a boiling temperature in water alone, seems to be in perfect combination with it, though without acquiring any saccharine product; and since it is not apparent how any combination with water should produce such an important change of properties *.

Of the varieties of sugar, that of the sugar cane may be considered as the species in its purest, and best defined form. Its properties, therefore, are first to be stated.

When pure its taste is perfectly sweet, free from any pe-

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* Annals of Philosophy, vol. i. p. 65. v. p. 55. vi p. 425. Annales de Chimie, tom. 82.

culiar flavour; it is inodorous and of a white colour; and in the state in which it is usually prepared, is composed of brilliant grains; the sugar from different vegetables, however, often retains extractive, mucilaginous, or oily matter, from which it derives taste, flavour, and other qualities.

Sugar is abundantly soluble in water: at the temperature of 50 it does not require more than its own weight to dissolve it: at a higher temperature the quantity dissolved is greater; and at 212° the water retains any quantity in solution. The consistence of a strong solution is thick and viscid. In pharmacy it is named Syrup, and different syrups are prepared from vegetable juices, or vegetable infusions, by adding the requisite proportion of sugar.

Sugar crystallizes from its saturated solution: the form of the crystals is a prism of four or six sides, bevelled at each extremity, or sometimes acuminated by three planes. It does not, according to Berzelius, contain more than 1 per cent. of water of crystallization, but contains in its common state about 5 per cent of water in intimate combination.

Sugar is also soluble in alkohol, and the solution affords crystals on evaporation. In the vegetable analysis, this solution is employed to extract sugar from those vegetable products which contain it in small quantity, as it frees it from the mucilage which adheres to it; and by slow crystallization it may be separated from any other principle which the alkohol had dissolved. By this process Margraaf obtained pure sugar from a number of vegetables.

When exposed to heat, sugar is blackened, swells, and burns to a coal; and if the heat be high, this is accompanied with flame. The products of its combustion are water and carbonic acid.

The fixed alkalis combine with sugar in solution in water: the alkaline properties, as Lowitz observed, are little altered by the combination, even when a large quantity of sugar is used, and the alkali is boiled with it. The sweet taste of the sugar is nearly destroyed, but on adding sulphuric acid, and precipitating the sulphate by alkohol, the sweetness is restored *. The compound of sugar and potash appears not to be soluble in alkohol, though both its ingredients are; Mr Cruickshank having found, that when alkohol was added to a solution of sugar and pure potash, which had been boiled to the consistence of a syrup, no union took place.

The action of the alkaline earths on sugar is similar to that of the alkalis. In boiling a solution of sugar with a little lime, Mr Cruickshank found, that the lime combined with the sugar, and communicated to it bitterness and astringency: by evaporation the liquid was reduced to a semitransparent substance, tenacious, and having a rough bitter taste mixed with a degree of sweetness. On adding alkohol to the solution, a precipitate in white flakes was formed, which appeared to be a combination of sugar with lime. Sulphuric acid added to the solution, precipitated the lime in the state of sulphate, and in a great measure restored the natural taste †. Lowitz had observed, that sugar communicates a greater degree of solubility to lime, equal parts of them being boiled together in water. In inspissating this compound, a white mass was obtained extremely acrid and caustic. The solution in boiling becomes thick and turbid, lime being precipitated; but as it cools, the lime is redissolved. Alkohol precipitates the lime; the alkaline carbonates decompose it by forming carbonate of lime; and it appears to be decomposed on exposure to the air, from absorption of carbonic acid, minute crystals being formed, and the sweetness of the sugar being restored ‡. Mr Cameron, who also observed this property in sugar of rendering lime more soluble in water, found the same effect to be produced on strontites; and this earth

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[*] Cruickshank, Rollo on Diabetes, p. 461. [†] Ibid. p. 461.

[‡] Journal de Physique, tom. xlii. p. 460.

was likewise separated from its combination with the sugar, both by the alkalis and the acids. Magnesia is very little soluble in a saccharine solution; and the solubility of barytes he found not to be increased by sugar *.

Sugar combines with some of the metallic oxides, particularly oxide of lead: it decomposes several metallic salts; and, according to Vogel, reduces the oxide which is their base in general to a lower degree of oxidation †.

Sugar is decomposed by the acids. Sulphuric acid blackens it, by causing an evolution of charcoal, while the remaining principles of the sugar enter into new combinations, forming water, and probably some of the vegetable acids. Nitric acid yields oxygen to it, and converts it into an acid, which, from being abundantly formed by the oxygenation of sugar, was at one time named Saccharine acid, and which Scheele demonstrated to be oxalic acid. The process consists in pouring six parts of nitric acid on one part of sugar in coarse powder, and applying a moderate heat; an effervescence takes place, and nitrous acid vapour is disengaged: the application of the heat is continued until this ceases, and in the remaining liquid prismatic crystals soon form, which consist of oxalic acid, and which, according to Cruickshank's experiments, amount to rather more than half the weight of the sugar. There remains an uncrystallizable liquid, containing malic acid. According to Vauquelin, when a little sugar is put into liquid oxymuriatic acid, it is converted into citric acid; but if oxymuriatic gas be transmitted through a solution of sugar, the liquid when evaporated affords a residuum; presenting all the characters of caramel, or sugar imperfectly burnt ‡.

The products of the destructive distillation of sugar in

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* Nicholson's Journal, vol. xviii. p. 10.

† Annals of Philosophy, vol. vii. p. 42.

‡ Annales de Chimie, tom. vi. p. 220.

close vessels, are pyro-mucous acid diluted with water, and a little empyreumatic oil; carbonic acid, and carburetted hydrogen gases, are disengaged; and the residuum is charcoal. The proportion of acid is larger than that obtained from the decomposition of gum. Cruickshank found *, that when saturated with lime it gave no indication of ammonia, as the acid from gum does; neither did the charcoal contain any lime; neither nitrogen nor lime therefore enters into the composition of sugar, and it is to be regarded as a compound merely of carbon, hydrogen, and oxygen. It differs from gum in the absence of nitrogen and lime; and from fecula probably in the proportion of oxygen being larger, and of carbon being less; since in the process by which fecula is converted into sugar, oxygen is absorbed and carbonic acid evolved. The proportions of its elements, as determined by Lavoisier, from the changes it suffers in the process of fermentation, are 64 of oxygen, 28 of carbon, and 8 of hydrogen; but these were inferred from results so complicated, that they cannot be regarded as certain. Gay Lussac and Thenard give as the proportions, carbon 42.47, oxygen 50.63, hydrogen 6.90. Berzelius assigns proportions very nearly the same, carbon 42.704, oxygen 50.405, hydrogen 6.891.

From the differences which exist in the composition of gum, fecula, and sugar, may be traced their successive formation in the process of vegetation. The sap is composed of vegetable matter, mixed with salts which have lime for their base. Mucilage or gum, which seems to be the first product from it, consists of carbon, hydrogen, and oxygen, the general principles of vegetable matter, combined with lime. By a further elaboration the lime seems to be abstracted, and the carbon, oxygen, and hydrogen, brought into union, form the fecula: and this again, by a change in the proportions of its principles, and particularly by an

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* Rollo on Diabetes, p. 466.

addition of oxygen, or abstraction of carbon, is changed into sugar.

A fact apparently singular was observed by some of the German chemists, in their experiments on the production of sugar,—that the exclusion of light favours its production,—so much so, that a plant, the roots or stems of which are sweet while the light is excluded, loses this sweetness when the light is admitted *. The exclusion of light in a growing vegetable favours the accumulation of oxygen, and therefore, according to the view now given, will favour the conversion of fecula into sugar. It may be added, that in vegetables the saccharine matter seems to be formed chiefly in the parts secluded from light, as it is most abundant in the roots, and in the sap rising from them, while it is scarcely discovered in the leaves. Sugar is formed, however, in the fruit of vegetables; and with regard to this Achard mentions a fact which appears at first contradictory,—that the formation of the sugar is promoted by light; this is indeed well known with respect to the maturation of fruits. Instead, however, of furnishing any exception to this view of the formation of sugar in the vegetable system, it confirms it; for it is not fecula, but an acid juice, which in the fruit is converted into sugar; and this conversion seems to be effected, as might *a priori* be inferred, by an abstraction of oxygen from the acid.

Mr Cruickshank endeavoured to convert sugar into gum, by the action of substances which might partially abstract its oxygen. He added to a portion of syrup, which filled an inverted jar placed over mercury, a little phosphuret of lime; a considerable production of phosphoric gas almost immediately took place; at the end of eight days the syrup had no sensible sweet taste, but rather a bitter astringent one; when filtered, alkohol produced a copious white precipitate in flakes, very much resembling mucilage separated from water by the same substance. When phosphuret of lime was added to a solution of sugar in alkohol, which was exposed to the air so that the alkohol evaporated, on adding distilled water, and filtering the liquor, it afforded by evaporation a substance extremely tenacious, which had the appearance of gum arabic; its taste was bitter, with a very slight degree of sweetness; when thrown upon a red-hot iron, it burned like gum, and left a bulky and insipid charcoal. The sugar therefore was, in these experiments, converted into a substance resembling gum: and that this was effected by the abstraction of oxygen, is probable, as Cruickshank adds, from the nature of the substance employed, and the change which it was found to have undergone; for there are few substances which have so strong a tendency to combine with oxygen, as the phosphuret of lime *.

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* Nicholson's Journal, 4to, vol. iii. p. 242. 288.

A singular fact with regard to this subject was communicated to me by Mr Cameron of Glasgow,—that a solution of sugar may be made to assume the tenacity and thick consistence of strong mucilage. The experiment consists in adding 1½ lb. of syrup (made with 1 part of water to 2 of sugar) to a gallon of water, in a stone bottle, mixing them by agitation, stopping the bottle closely, and placing it in a temperature of about 50, for three or four days. In this time it becomes gelatinous, still retaining its saccharine taste, but which in the course of a week or two it loses. By boiling it, it loses its gelatinous form, and assumes that of strong mucilage of gum senegal. I have kept it in this state for a considerable time. It is not improbable, that a slight change is produced in the combination of the principles of the saccharine matter, so as to bring it to the state of mucilage: and a curious fact observed by Mr Cameron, that the experiment succeeded only with unrefined sugar, accords with this; unrefined sugar probably

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* Rollo on Diabetes, p. 459.

containing a small portion of the lime employed in the process of preparing it, and lime being essential to the constitution of mucilage or gum. A solution of sugar boiled with a little lime, forms a very tenacious liquid.

The Sugar of the Grape, it has already been remarked, was pointed out by Proust as essentially distinct from that of the sugar cane. They differ considerably in their properties. The grape sugar consolidates in small granular masses, which have a radiated structure, similar to the spherical concretions in honey, and this is the only kind of crystallization it can be made to assume. When the syrup adhering to this is removed, the sugar may be obtained in a dry powder perfectly white, but it cannot be brought like common sugar into an indurated form; its sweetness is inferior to that of the other, and is accompanied with a kind of coolness of taste; it is less soluble in water; and though it dissolves entirely in alkohol, it separates from it more readily, and always consolidates in granular concretions, without any regular figure. It is more disposed to pass into fermentation, its solution fermenting spontaneously at the proper temperature, while the solution of common sugar requires the addition of a ferment. According to Th. Saussure, it differs too in chemical constitution from the sugar of the cane, the latter containing a larger proportion of carbon. He obtained, by the analysis of cane sugar, results nearly the same as those given by Gay Lussac and Thenard, that is, between 42 and 43 of carbon, with oxygen and hydrogen in the proportion forming water; while the proportions from the analysis of the sugar of the grape, were carbon 36.71, oxygen 56.51, hydrogen 6.78, leaving, besides the smaller proportion of carbon, an excess of oxygen to the hydrogen above that forming water, of 5.29 *.

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* Annals of Philosophy, vol. vi. p. 424.

Beet sugar is analogous to the sugar of the cane, and is even like it capable of crystallizing. According to Th. Saussure, its composition too is so far similar, that it contains the larger proportion of carbon which distinguishes the other. Maple sugar is inferior to the sugar of the cane in sweetness, and in solubility in water. The sugar obtained from starch is of all these most analogous to grape sugar; being, as Saussure has remarked, perfectly similar to it in its cool taste and inferior sweetness, in melting at the temperature of boiling water, in crystallizing from its watery solution in spherical masses, and in passing spontaneously into the vinous fermentation. And its analysis affords a composition almost precisely the same, being carbon 37.29, oxygen 55.87, hydrogen 6.84.

The nature of the liquid uncrystallizable sugar which is found in many fruits, from which the concrete sugar separates, and of which the Molasses or Treacle from the saccharine juice of the cane is an example, is not well determined. It is probably a farther modification of that difference which constitutes the distinction between these other varieties of sugar. Like them it is distinguished by the facility with which it passes into fermentation. Or it may have some degree of intermixture affecting its properties.

Sugar is of importance as a substance nutritious and generally agreeable in taste. It exists in the greater part of the vegetable substances used as articles of diet, and appears, from some facts with regard to its use, to be highly nutritive. Even animals, when partially supplied with it, it has been observed in the West Indies, become fat and vigorous, as during the time of the sugar harvest, though they are then kept almost constantly at work. By its antiseptic power it preserves a number of substances from putrefaction, and hence, in confectionary and in pharmacy, it is used in the preparation of conserves, syrups, and similar compositions. It is also used in the composition of varnishes, of ink, and of some pigments, to communicate lustre.

There are some substances of a saccharine nature, differing in their chemical properties from pure sugar, which may be noticed under this section.

Manna is a secreted juice, afforded by several vegetables, but in largest quantity by several species of ash, particularly the Fraxinus ornus, which are cultivated in Sicily and Calabria for its production. It exudes spontaneously from the bark, but is obtained more copiously by incisions in the stem and branches. When it flows slowly it is more pure: it is collected on straws or chips of wood, and forms Flake manna: when it flows more abundantly it is less pure, and forms the common manna of commerce.

The purest manna is in pieces of a texture somewhat granulated, having a taste sweet, but rather disagreeable. It is soluble in water and in alkohol: its solution in hot alkohol deposites, on cooling, an abundant congeries of light white crystalline needles, perfectly sweet; the residual liquor affords by evaporation a darker and somewhat tenacious extract. It has been supposed to contain, besides saccharine matter, mucilage and extractive matter, from which its taste and peculiar qualities are believed to be derived; but, according to Proust,[*] these are not to be discerned in it, and it is merely a peculiar species of soft sugar. It is affirmed by Chaptal, that when its solution in water is boiled with lime, clarified with the white of an egg, and concentrated by evaporation, it affords crystals of sugar. According to Fourcroy and Vauquelin, it is converted into oxalic acid by the action of nitric acid, without affording any trace of saccho-lactic acid, if care has been taken to free it from mucilage by the action of alkohol. Proust, on the contrary, affirms that it is a characteristic property of it to yield both oxalic and saccho-lactic acids.

Honey is another vegetable product, similar in many of its properties to sugar: it is formed in a number of vegetables: it is collected by the bee; and many other insects feed upon it. It is always formed in the flower, chiefly at the base of the pistil, and is exposed, frequently by a complicated arrangement, to the atmospheric air.

The nature of this product is not well ascertained. It evidently contains a large quantity of saccharine matter; with this it has been supposed a portion of mucilage is combined, from which it derives its softness and viscosity: its peculiar taste and smell, as well as other qualities which honey from particular plants sometimes has, are probably owing to extractive matter, or essential oil, with which it may be impregnated. It is soluble in water: by the action of nitric acid it is converted into oxalic acid, one ounce affording, according to Cruickshank's experiments, 4 drachms, 4 grains of acid, a quantity little less than that afforded by sugar.

Lowitz found, that by adding charcoal to honey dissolved in water, he deprived it of its peculiar smell, taste, and colour: but on evaporating the solution, it resumed its colour, and did not shew any disposition to crystallize. On the inspissated liquid, however, being allowed to stand for two months, small masses formed in it of a crystallized appearance: these were obtained pure by diluting with alkohol, which dissolved the glutinous matter; when dried they formed a powder, which had an agreeable sweet taste.

The granulated consistence of white honey appearing to arise from the concretion of its saccharine part, he endeavoured to separate that part by the action of alkohol. He thus procured from 12 ounces of honey, 3 ounces of saccharine matter, which still, however, appeared to contain some heterogeneous substance not soluble in alkohol. He therefore boiled pure alkohol on the whole of it: the saccharine part was dissolved, while an insoluble matter remained on the filter, through which the liquor had passed while hot. This liquor, after having stood for some days, deposited the saccharine matter in small spherical masses, which accumulating, formed a crust firm and white. This matter, however, Lowitz was unable to crystallize, though its texture showed a kind of crystalline arrangement. This sugar of honey he found to differ from common sugar in the changes which it suffers from certain re-agents, particularly from the alkalis and alkaline earths. If lime-water be added to its watery solution, a brown colour is acquired. Quicklime added to the solution while hot, produced strong effervescence, and the mixture became of a dark-brown colour: and by continuing to add lime, the saccharine matter was decomposed. If the solution of honey and quicklime is thickened by evaporation, after its brown colour is removed by charcoal, a transparent matter is procured of a light yellow colour, which resembles gum arabic, but has a bitter taste. The fixed alkalis produce changes on honey, and on the saccharine matter procured from it, the same as those from the action of lime. Ammonia produces similar effects, but more slowly, and only when its action is promoted by heat *.

Cavezzali gave a process by which the sugar of honey is obtained crystallized. It consists in clarifying white honey, by applying a moderate heat, and removing the scum from its surface, then adding to it egg-shells (which consist principally of carbonate of lime) in powder; an effervescence takes place; the addition is continued to saturation, and the liquid set aside. A thick scum which forms on its surface is removed, and some mucilaginous flocculi are separated by filtration. A clear syrup is thus procured, free from the sharpness of the honey. At the end of four months, a crystalline crust had been deposited of a red colour, which attracted humidity; but the colour was

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* Journal de Physique, tom. xlii. p. 456.

removed by washing with alkohol, and after this operation it remained dry *.

Some experiments on honey have been lately made by Guilbert. When agitated with the fourth of its weight of water, he found that it became liquid. Thrown on a filtre, a portion passed through having the appearance of syrup, and a kind of paste remained on the filtre, in quantity about $\frac{1}{15}$ of the honey. This matter, washed with alkohol, lost its yellow colour, became dry and farinaceous, and scarcely sweet; it was soluble in syrup and in alkohol by heat: it was also soluble in four parts of cold water: it melts from a moderate heat: it affords, when acted on by nitric acid, oxalic acid. According to Guilbert, it has a purgative quality, which does not belong to the syrup, and this quality in honey must therefore be derived from it †.

Proust distinguished two species of honey, as well as of sugar; the one, the common yellow honey, of a uniform consistence and viscid; the other, the granulated white honey, which becomes solid, and assumes the form of small spherical masses. From the white granulated honey he obtained, by the action of alkohol, a saccharine powder of an agreeable, cool, and sweet taste, which he regards as nearly the same with the soft sugar of grape ‡. The other appears to be a liquid uncrystallizable sugar, with which the concrete variety is more or less mixed.

The saccharine matter formed in certain morbid states of the animal economy, giving rise to the disease named Diabetes, appears similar in many of its properties to the sugar of honey. It suffers nearly the same change from lime: in the experiments made on it by Nicolas, when a little lime was added to its solution, and the whole boiled, on afterwards clarifying it with the white of an egg, the liquor was found to have assumed a reddish-brown colour,

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* Annales de Chimie, tom. xxxix. p. 110.

† Ibid. tom. lxxxii. p. 109.

‡ Ibid. tom. lvii. p. 157. &c.

had lost its sweetness, and become acrid; and when the lime was separated from the combination by the addition of an acid, the sweetness was not restored *. This is the kind of change the sugar of honey suffers from lime, and is different from that which pure sugar undergoes. Cruickshank found, that the saccharine extract formed in diabetes is convertible into oxalic acid by the action of nitric acid †; a property which belongs to the sugar of honey as well as to pure sugar.

SECT. V.—OF GLUTEN.

ALONG with the fecula and saccharine matter which compose the principal part of the nutritive grains, there exists a substance, approaching in its characters to animal matter. From its resemblance to the animal principle formerly named Gluten, it has received the name of Vegetable Gluten. It has been believed likewise to be contained in the juices of plants; but it is more easily separated from the farina of the nutritive grains, and it is from the gluten extracted in this way that its characters are derived. Its existence was pointed out, more than seventy years ago, by Beccaria, to whom we are indebted for the simple analysis of the nutritive grains by which it is obtained.

In obtaining the fecula of wheat, by kneading the flour made into a paste with water in the hand, or in a coarse linen bag, the fecula is carried off suspended in the water, and the sugar and other soluble principles are dissolved. There remains at length a soft viscous substance, of a fibrous texture, possessing great tenacity and elasticity. It

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* Annales de Chimie, tom. xliv. p. 65.

† Rollo on Diabetes, p. 429.

is this which is denominated Gluten. It is obtained in largest quantity from wheat; the quantity, on an average, amounting, when dry, to about a twelfth part of the weight of the flour of that grain; and taking into account the weight of the water with which it combines in its extraction, it varies, according to Beccaria, from a third to a fifth of the weight of the flour. Sir H. Davy found the flour of the wheat of this country to consist of from 20 to 24 of gluten, with from 70 to 77 of starch; the wheat of warm countries, he states, contains in general a larger proportion *. Gluten is contained in much smaller quantity in the other nutritive grains, and can, indeed, be scarcely extracted from a number of them. Sir H. Davy found barley to consist of 79 of starch, 6 of gluten, and 7 of saccharine matter, with 8 of husk; and from rye 61 of starch, with 5 of gluten. Einhoff had obtained analogous results from both these grains. Beccaria found traces of it in maize. Rice consists chiefly of starch; but, according to Braconnot, it contains also a portion of vegeto-animal matter, which is analogous to gluten †. And Fourcroy and Vauquelin found, that a principle possessing the characters of animal matter, and therefore probably also analogous to gluten, exists in garden-beans and lupines. There are no traces of it in the potatoe, or other nutritive roots. It has been supposed to be contained in the juices of plants. Rouelle had observed, that the juices of the fresh leaves of a number of vegetables deposited, on standing, a matter which, from its colour, he named Green Fecula; and in this substance he discovered the existence of a principle which he considered as analogous to the gluten of wheat.

The gluten obtained in the analysis of wheat flour, by the method above described, is a solid viscous substance,

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* Elements of Agricultural Chemistry, p. 125.

† Annals of Philosophy, vol. x. p. 192.

extremely tenacious, so that it can be drawn out to a great length, and moulded into any form; it is also highly elastic, so that it quickly resumes when left to itself its former volume: its texture is distinctly fibrous. It has scarcely any taste; its odour is faint: its colour is greyish, and, when dried, it is semi-transparent, having some resemblance to glue in its appearance. In its soft state it is extremely adhesive to the touch, and has, from this property, been used as the basis of cement, for uniting fragments of porcelain or glass.

When exposed to the air, gluten remains for some time soft, acquiring a darker colour. If exposed to a dry and warm atmosphere, it dries slowly, and loses its ductility and elasticity. This induration of it is more complete, when a moderate heat is slowly applied to it; it may then be rendered hard and brittle. But in a humid atmosphere soft gluten retains its softness, and soon passes into putrefaction, swelling, and acquiring an offensive odour,—changes which are accompanied with the formation of ammonia, acetic acid, and an oily matter [*]. If it has not been entirely deprived of the fecula of the wheat, this, according to Macquer's observations, suffers the acetous fermentation; and the re-action of the small portion of acid, with the slow action of the air and water, converts the gluten into a substance, which, as Rouelle remarked, has a near resemblance to cheese, and which, by the addition of salt, may be preserved in that state [†].

When kept immersed under water, a formation of acetous acid takes place, and ammonia is also formed, which combines with this acid, though not in quantity sufficient to saturate it. This evolution of acetic acid appears, as Vauquelin has remarked, to check the progress of putrefaction;

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[*] Annales de Chimie, tom. xxxviii. p. 259.

[†] Fourcroy's System, vol. vii. p. 417.

and, by its action, a portion of the gluten is dissolved by the water *. In this state of solution, it gradually putrefies, separating in mucous pellicles.

The gluten that remains undissolved, after this kind of fermentation which it has suffered, if immersed anew in water, begins again to ferment, disengages carbonic acid, becomes of a purple colour, and emits a fœtid odour, similar to that from putrid animal membrane. After some months of this slow putrefaction, it has acquired a brown colour, exhales only a faint smell, is much diminished in volume and quantity; when dried, it forms masses, which soften under the finger like wax, melt and burn with flame; it is soluble in alkohol, which it colours brown; a portion remains undissolved in the state of a powder, inodorous, insipid, and similar to charcoal powder, but burning with an acrid odour, and affording ashes, in which iron and silex exist. In this series of changes, part of the nitrogen and hydrogen of the gluten unite to form ammonia; part of its carbon forms, with oxygen, carbonic acid; another portion of carbon, with hydrogen, form the unctuous matter; and the remaining elements united, form the residuum †.

It is doubtful if gluten is soluble in pure water. When water is allowed to remain over it, its transparency is impaired, and a mucous matter appears to be dissolved, or rather suspended in it: by filtration it may be rendered limpid: when heated, a glutinous matter separates in flocculi: and a precipitate is thrown down by oxymuriatic acid, and by tannin. But it is not certain that these phenomena depend on the presence of pure gluten; it is probable they are connected with the changes in composition which it has suffered, and probably with the production of acetous acid, from its partial decomposition. When

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* Annales de Chimie, tom. xxxviii. p. 259.

† Annales du Museum d'Histoire Naturelle, tom. vii. p. 4.

water is boiled on gluten, it contracts, becomes more solid, and loses its tenacity and ductility.

Gluten is insoluble in alkohol: alkohol even precipitates the small portion of it which water, when it has been macerated on it, holds dissolved. If gluten, however, which has been kept for some time under water, so as to have passed into the acid fermentation, be triturated with alkohol, it is partially dissolved, and a liquid of a thick consistence formed. If more alkohol be added to this, part of the gluten is precipitated, but a portion remains in solution, and by filtration forms a transparent liquid. By evaporation the gluten is obtained dry, brittle, and shining. Cadet, by whom these experiments were made, has remarked, that the thick solution of fermented gluten in alkohol forms an excellent varnish, as it is transparent, adheres strongly, has a degree of elasticity, and does not scale off. A similar varnish is obtained by dissolving gluten in acetous acid; that formed by alkohol is preferable, but both have the imperfection of being affected by humidity. This latter solution also forms a cement for porcelain, and a basis for paints *.

Gluten is dissolved by alkaline solutions, when their action is aided by heat. On the addition of an acid to the solution, the glutinous matter is precipitated, but so far changed as to be no longer elastic. In a concentrated state, the alkalis decompose it, and form a kind of soap, while there is also a production of ammonia.

The changes produced in gluten by the acids are different according to the nature of the acid, and its concentration or dilution. The weaker acids, as the acetic, dissolve it, though not without some change, as, during the solution, a portion of ammonia is formed; and when the acid is neutralized by an alkali, the gluten is precipitated with the loss of its ductility: Fourcroy affirmed, however,

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* Philosophical Magazine, vol. xiii. p. 9.

that it is precipitated with its properties unaltered *. When it has undergone the slight fermentation which it suffers when kept under water, it is still more soluble in acetic acid; and a portion of it appears, from Vauquelin's experiments, to exist dissolved in the sour liquor obtained in the preparation of starch from wheat, probably by the medium of the acetous acid, and in consequence of this slight change †. Hence, as he has observed, the necessity, in the preparation of starch from wheat, to allow the liquor above the fecula to run into the acetous fermentation, and in its acid state to remain over it for some time; the acetous acid dissolving the portion of gluten which adheres to the starch, and thus rendering it more pure, of a whiter and more brilliant colour, and more loose and dry; while in the preparation of starch from the potatoe, or from other roots or grains which do not contain gluten, this is not requisite.

Sulphuric acid blackens gluten, and causes a formation of acetic acid and of ammonia, with an evolution of carburetted hydrogen. Nitric acid disengages from it nitrogen gas, and gives rise to the production of oxalic and malic acids. Muriatic acid acts on it slowly, and in a manner somewhat similar to the acetic. Oxymuriatic acid softens gluten, and changes it into a yellowish flocculent matter. It also precipitates it from any combinations in which it is in a state of solution, and thus affords a test by which its presence may be recognised. Dr Bostock has pointed out some other tests. Precipitates are thrown down from water macerated on it by acetate and super-acetate of lead. Nitrate of mercury causes a precipitate to subside quickly, and the liquid above assumes a pink colour. It is not precipitated by silicated potash, but gives a copious precipitate with infusion of galls.

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* Annales du Museum d'Histoire Naturelle, tom. vii. p. 4.

† Annales de Chimie, tom. xxxviii. p. 259. 261.

Gluten presents a peculiarity in its decomposition by heat; the products being the same as those of animal matter. When exposed to a moderate heat, it swells: if placed on burning fuel, it becomes soft or semi-fluid, and burns with a fœtid odour. If subjected to destructive distillation, it affords carbonate of ammonia, partly concrete, partly in solution in water, a large quantity of a thick empyreumatic oil, and a little prussic acid: there is disengaged also carburetted hydrogen gas; and the remaining charcoal is of difficult incineration. From the production of ammonia, it is obvious that nitrogen enters into the composition of gluten; from the large portion of oil which it affords, it must contain much hydrogen; while none of the products indicate the presence of oxygen in any considerable proportion. Phosphorus also appears to exist in its composition. Vauquelin found, that the liquor formed in the preparation of starch from wheat, contained a portion of phosphoric acid in combination with lime, probably derived from the gluten of the wheat; and the phosphate of lime found by the same chemist to exist in the ashes of wheat-flour, has probably the same origin. In its analysis, therefore, gluten presents all the characters of animal matter, as it does also in being liable to putrefaction, and in affording nitrogen from the action of nitric acid.

Gluten appears to have the property of promoting fermentation; and the action of yeast in exciting this process, has been supposed to depend on the gluten it contains. Vauquelin remarked, that the water in which gluten has been macerated, converts sugar into excellent vinegar without effervescence, and without the contact of the air *.

From the nature of this principle, it must contribute to the nutritious quality of the grains in which it exists, as containing all the qualities required for animal nutrition: hence the superiority of wheat, which contains it in so

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* Annales du Museum d'Histoire Naturelle, tom. vii. p. 4.

large a proportion to the other nutritive grains. It is on the presence of this principle, too, that the superior quality of bread from wheat, compared with that from other grains or roots, depends, as Beccaria remarked. The flour of these forms with water a solid friable paste; while the flour of wheat forms a paste that is ductile and elastic, the gluten forming the body of the paste through which the fecula and saccharine matter are diffused; and when the slight fermentation which it suffers, probably from changes in the saccharine matter favoured by the presence of the gluten, takes place, this paste becomes spongy and porous, from the disengagement of the carbonic acid gas, while it still retains in some measure its elasticity; hence the lightness and porosity of well-baked wheaten bread. Bread possessing these qualities cannot be prepared from the flour of oats, barley, rye, or rice, or from any of the nutritive roots, as in all of these the quantity of gluten is less considerable, or entirely wanting.

The experiments on the analysis of the principal nutritive grains by Fourcroy and Vauquelin, though imperfect, confirm in a great measure preceding results. Besides fecula, sugar, and gluten, they found them to contain portions of phosphate of lime, potash, and magnesia, and oxide of iron. Some liguminous plants, particularly lupines, they found, contain neither fecula nor sugar *. Some experimental researches on the same subject have more lately been given by Vogel. The flour of wheat (triticum hybernum) he found to be composed of fecula 68, gluten 24, gummy sugar 8.6, vegetable albumen 1.5. The flour of the oat consists of fecula 59, albumen 4.3, gum 3.5, sugar and bitter principle 8.25, oil 2, with fibrous matter. Rice contains fecula 96, sugar 1, oil 1.5, and albumen 0.2 †.

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* Annales du Museum, &c. tom. vii. Philosophical Magazine, vol. xxv.

† Annals of Philosophy, vol. xi. p. 514.

The expressed juices of a number of plants of the cruciform kind, contain a principle analogous to animal matter, in being liable to putrefaction, and evolving ammonia during its decomposition. Rouelle regarded this as a variety of vegetable gluten, and he supposed it to form the basis of the green fecula which is contained in the expressed juices of many plants. Fourcroy, finding that this principle exists in solution in these juices, that it is separated by coagulation by heat, and by acids, while it is dissolved by alkalis, properties in which it approaches to the proximate principle of animal matter, denominated Albumen,—considered it as different from gluten, and gave it the name of Vegetable Albumen *. Proust called in question the opinion of Fourcroy, and revived that of Rouelle. The principle which is the subject of this diversity of opinion, wants some of the physical characters of gluten, but this may be owing to the form in which it is obtained; it approaches to it in several chemical characters, and on the whole may with most probability be regarded as a variety of it.

If scurvy grass, cabbage, cresses, or horse-radish, in the recent state, be subjected to pressure, the juice that is obtained is somewhat turbid; but, on raising its temperature to between 170° and 212°, flocculi are formed, which are diffused through the liquid, or subside from it, and are easily separated by filtration. It is this matter which Fourcroy considered as albumen, or which Rouelle and Proust regarded as analogous to gluten.

In its separation, part of the green colouring matter of the plant, in a state somewhat similar to fecula, and sometimes of a resinous nature, adheres to it; but Fourcroy succeeded in separating this, by the following process: The

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* Annales de Chimie, tom. iii. p. 252.

juice of young cresses being passed through a paper filtre, left the grosser fecula suspended in it on the filtre: the filtered liquid, though limpid, was of a green colour; but after exposure to the air for two hours, it became turbid, and, on being filtered again, became limpid, leaving a quantity of green fecula on the filtre. On plunging the vessel containing it into a bath of boiling water, it became turbid, and a whitish coagulated matter separated from it. Another portion of the juice, exposed to the air for two days, deposited similar flocculi; and they were also separated by adding sulphuric acid *.

This concrete matter was found by Fourcroy to be insoluble in water, even when boiling: it gave a green tinge to paper coloured with mallow flowers: the alkalis dissolved it readily: macerated in water, it exhaled a fœtid ammoniacal odour, and passed into putrefaction: exposed to a dry and warm atmosphere, after having been pressed between bibulous paper, it acquired a degree of ductility and transparency similar to that of glue: subjected to distillation, it afforded a large portion of ammonia. These characters are equivocal, if regarded as serving to determine that this is a principle distinct from gluten, and analogous to albumen. The most characteristic property of this last substance is its being coagulated by heat; and so far the principle contained in these vegetable juices resembles albumen. But in the history of gluten it has appeared, that, by the medium of certain re-agents, of a small quantity, for example, of acetous acid, it may exist in solution in water; and that, when this liquor is heated, the gluten separates in flakes. Proust has remarked, too, that the coagulation of this matter from the vegetable juices takes place at 145° of Fahrenheit, while albumen does not at that temperature experience any change: and farther, that when the vegetable juice is largely diluted with water, as

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* Annales de Chimie, tom. iii. p. 257.

with 20 parts, the coagulation still takes place, when the temperature is raised; while animal albumen, equally diluted, does not coagulate when heated, the liquid becoming opalescent; and no flocculi separate, even when the liquor is boiled *.

This vegetable principle is coagulated by acids, in which it resembles albumen. But the gluten of vegetables is also precipitated by some of the acids. Alkohol throws it down in the state of an opaque whitish powder; while it precipitates animal albumen in light flocculi. It is dissolved by alkalis. But the gluten of vegetables is also dissolved by the alkalis.

The other characters enumerated by Fourcroy, as serving to connect this substance with albumen, are less appropriate. Insolubility in water, being liable to putrefaction, and evolving ammonia, either when suffering this change, or when decomposed by heat, are characters belonging to vegetable gluten, as well as to animal albumen.

One property assigned to it by this chemist, which is peculiar to albumen, is changing some of the vegetable colours, as that of mallows, to a green. But according to Proust, when it is washed it does not produce this change, and the juices in which it is contained have no such property; some of them even, as the juice of cabbage or hemlock, render litmus red. When the vegetable principle does possess this property, therefore, it is probably owing to the evolution of ammonia. Proust has pointed out other properties in which this principle differs from albumen, such as that of being precipitated by a number of neutral salts, which do not render albumen turbid; and being more liable to spontaneous decomposition than albumen.

One circumstance which confirms the conclusion, that this matter is vegetable gluten, disguised by the state in which it exists, is, that it exists in the water employed in

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* Philosophical Magazine, vol. xvii. p. 25.

preparing the starch from wheat-flour, and is separated from it by coagulation by heat, as Fourcroy has remarked; in the same manner as from the expressed juices. It is more probable, that a portion of the gluten known to exist in this flour shall be in solution, and be the substance separated in this manner, than that it shall be a distinct principle, especially as it is proved, that the solubility of gluten is promoted by the action of acetic acid, and that this acid is contained in the liquor formed in the preparation of starch. Proust has accordingly observed, that this matter suffers changes like gluten: kept in a humid state, it forms acetic acid and ammonia, and, like gluten, acquires the odour and taste of cheese [*].

That this principle should have the physical qualities of gluten, is not to be expected; for if a different process be followed with regard to the farina of wheat, than that usually employed to extract its gluten,—if, instead of being made into a paste and kneaded with water, it be diffused at once in a large quantity of water, the separation of the fecula no longer properly takes place, and the gluten is not obtained. It then probably exists in the water in the same state as in the vegetable juices.

Some observations by Link shew, that vegetable albumen is very analogous to gluten; though he also remarks, that in many points there is a considerable resemblance between gluten itself and animal albumen [†].

According to Proust, this principle exists in a number of plants. It is found in the expressed juice of borrage, elder, and buckthorn; also, in grapes, quinces, apples, and other fruits; and in the acorn, chesnut, horse-chesnut, rice, barley, rye, pease, and beans of all kinds [‡]. Seguin has remarked, that it renders more susceptible of fermentation, the vegetables in which it is contained.

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[*] Annales du Museum d'Histoire Naturelle, tom. vii. p. 5.

[†] Annals of Philosophy, vol. vii. p. 455.

[‡] Philosophical Magazine, vol. xvii. p. 51.

SECT. VI.—OF ALBUMEN.

THOUGH the principle which has been named Vegetable Albumen, appears, from the observations in the preceding section, to be a variety of gluten, there is reason to admit the existence of a vegetable product, to which that name may with propriety be applied, as, in the greater number of its properties, it has a strict resemblance to animal albumen. It exists in the juice of a plant, a native of the Isle of France, the Carica papaya, and has been made the subject of experiment by Vauquelin *, and by Cadet †. Of all the products of the vegetable system, it is the one which approaches most nearly to animal matter; and it might indeed be regarded as a variety of it, if its origin were not known.

The juice which contains this principle issues from the tree white as milk: in a few minutes it coagulates; flocculi of a white matter separate, and float in a transparent liquid. The juice is diffused through all parts of the tree, but is most abundant in the fruit while unripe.

The experiments of Vauquelin were made upon this substance in three states: 1*st*, In the solid state to which it had been reduced by exposure to the sun; 2*dly*, In its natural state, it having been preserved in bottles well closed; and, 3*dly*, In the state of the natural juice, mixed with sugar to preserve it without alteration.

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* Annales de Chimie, tom. xliii. p. 267.; tom. xlix. p. 295.

† Ibid. tom. xlix. p. 250.

The juice inspissated by exposure to the sun, is of a yellowish white colour; some parts of it are of a pure white and semi-transparent. It is brittle and easily reduced to powder when it is dry: it melts easily in the mouth, impressing a singular taste, and exciting a copious discharge of saliva. It attracts humidity from the air, and changes into a viscid paste. It is dissolved by cold water, and more abundantly by warm water; a small quantity of a white matter only being left undissolved, which has an unctuous appearance, melts easily, and diffuses an odour similar to that of empyreumatic fat. Its concentrated solution becomes turbid, and coagulates on ebullition; but the whole of the dissolved matter does not separate, as a portion is precipitated by other re-agents. Alkohol added in large quantity to the watery solution of the juice, separates it completely, and without occasioning in it any alteration. Sulphuric, nitric, and muriatic acids, coagulate it abundantly; and a precipitation is occasioned by a number of metallic solutions, as those of quicksilver, silver, and lead. Exposed on burning fuel, it burns, decrepitating slightly, and diffusing a fœtid ammoniacal odour, as animal substances do. Subjected to destructive distillation, it gives much carbonate of ammonia; a thick black oil, the greater part of which falls to the bottom of a brown liquid, which is produced at the same time; carbonic acid and carburetted hydrogen gases are disengaged, and there remains a charcoal light, difficult to burn, and which leaves as ashes, a little earthy matter, consisting of lime and phosphate of lime. Distilled with weak nitric acid, it gives a large quantity of aërial fluid, consisting of carbonic acid and nitrogen: and in dissolving in the acid, it communicates to it a yellow colour and a very bitter taste. There is also formed a large quantity of prussic acid and oxalic acid. Lastly, it is liable to putrefaction: its watery solution decomposes when kept, and acquires a fœtid odour, as animal matter does.

With regard to the liquid juice, on opening the bottle in which it was preserved, an elastic fluid was disengaged with such violence, as to throw part of the liquid to a distance: this gas was ascertained, both by Cadet and Vauquelin, to be carbonic acid, produced no doubt by the decomposition of some principle contained in the juice. Masses of a white matter similar to cheese, floated in the liquor: these, in drying, assumed the semi-transparency of horn; the dried matter softened when heated, and exhaled a white vapour, with an odour similar to burnt unctuous matter: it dissolved abundantly in warm alkohol, from which it in part separated again in cooling. This matter, evidently sebaceous, appeared to Vauquelin to have originated in the decomposition of the juice itself.

The liquid part contained a principle which had properties similar to those of the inspissated juice, with a portion of acetic acid, originating probably from decomposition, as there is no sensible acidity in the inspissated juice. Its odour was fœtid and very disagreeable: it had a taste acid, bitter, and astringent. When rendered limpid by filtration, it had the same taste and smell. The acids coagulated it into a mass very thick, which had a great resemblance to the white of an egg, or to dried albumen. The action of oxymuriatic acid was rather peculiar: when added in a small quantity, it gave a rose colour; in a larger quantity a violet; and in a still larger quantity, it destroyed the colour: and as these phenomena did not appear when this acid was added to the inspissated juice, it follows, that some change must have taken place during the inspissation, subversive of the property of forming these colours. Pure potash formed, when added to the filtered juice, a precipitate of a white colour, and caused the exhalation of a strong ammoniacal odour. The liquor, when filtrated after this, still assumed a violet colour, from the addition of oxymuriatic acid. Alkohol added to the juice, evaporated until it had acquired the consistence of a syrup, produced a very abundant precipitate. The infusion of galls formed also a precipitate in large quantity.

The juice that had been preserved with the addition of sugar, had not suffered any particular change; for when the sugar was separated by alkohol, it presented the same properties as the concrete natural juice.

Vauquelin observes, that from these experiments there can be no doubt that the juice of this tree is composed principally of a matter which has all the characters of animal substances; and which approaches most nearly to those of albumen; since, when dry, it dissolves like it in water: the solution, like that of albumen, is coagulated by heat, by acids, alkalis, metallic solutions, infusion of galls, and alkohol; and, lastly, it affords by decomposition by heat, or by the action of nitric acid, the same products that animal substances the most completely characterized do. It may therefore properly receive the name of Vegetable Albumen. We cannot, adds Vauquelin, regard without interest a substance produced by a vegetable, presenting all the characters of animal matter; and we perceive from this example, that nature has given to certain species of plants, the power of forming combinations similar to those produced in the animal machine,—a fact indeed established, though undoubtedly in a less striking manner, by the production of gluten in the vegetable system.

SECT. VII.—OF CAOUTCHOUC, AND BIRDLIME.

Caoutchouc, sometimes named improperly Elastic Gum, is a vegetable product, which in several physical qualities, as well as in chemical relations, has some similarity to vegetable gluten, and which agrees with it and albumen, in approaching in composition to animal matter. It connects also the preceding principles with those which are to follow, and I therefore place it in this part of the arrangement.

This substance was brought from Spanish America, in the form of hollow spheres or bottles, in which state it is still imported into Europe. Condamine gave the information, that it is the inspissated juice of a tree of the family of Euphorbia, which has received the botanical name of Hævea guianensis, or Hævea caoutchouc. Incisions are made in the bark of this tree, and a milky juice exudes. This is applied, in successive coatings, over a mold of clay; is dried by exposure to the sun, and afterwards, by being placed in the smoke of burning fuel; when dry, the mold is broken and the fragments are extracted.

It has since been discovered, that caoutchouc is furnished by other plants, either the same, or with very slight variations of properties. It is obtained in large quantity from the Jatropha elastica, a native of South America. Dr Roxburgh has described another vegetable, a native of India, the Urceola elastica, which affords a juice, which when thickened has the properties of the American caoutchouc; and he has farther observed, that there are many trees, natives of the torrid zone, that yield a milky juice, possessing qualities nearly of the same nature; as Artocarpus integrifolia, Ficus Indica, Ficus religiosus, Hippomane biglandulosa, &c. *

Fourcroy procured specimens of the juice of the caoutchouc in the state in which it exists previous to its inspissation, from the island of Bourbon, from Cayenne, and the Brazils, and examined its properties. Each of these contained a white turbid liquor, of an unsupportable fœtid smell; in the midst of which was a white concrete matter, spongy at its surface, very elastic, of a soft and close texture. These concretions had the form of the bottles that

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* Nicholson's Journal, 4to, vol. iii. p. 455.

contained them, but were less in size: they had been deposited without evaporation, for the bottles were well closed, and had lost nothing. The juice, when exposed to the air, became speedily covered with a crust of elastic gum. In a vessel filled with oxygen gas, the liquid afforded an elastic pellicle more speedily, and a sensible absorption of gas took place. Alkohol separated flakes, and oxymuriatic acid immediately formed an elastic precipitate. From these experiments he concluded, that caoutchouc exists ready formed in the juice of the tree, and is capable of being separated in the concrete form; but that a portion also exists not sufficiently perfect to be deposited with its elastic property; that it acquires this, together with its inspissation, from the action of oxygen; and that by this operation, exposure to the atmosphere influences the concretion of caoutchouc in the usual process in which it is brought to the solid form *. Dr Roxburgh has likewise observed, that the milky fluid which oozes from incisions in the bark of the Urceola elastica, separates on exposure to the air into a firm elastic coagulum, and a watery liquid; the coagulum becoming of a darker colour from the action of the air, and being no longer soluble in the liquid, though before intimately blended with it. The purest caoutchouc Fourcroy supposes to be that which separates spontaneously from the juice in close vessels. It is white, or of a light fawn colour; and masses of it are sometimes met with in commerce nearly white.

The properties of caoutchouc have been determined principally from the state in which it exists in the elastic bottles imported into Europe. Its colour is light brown; its external surface is smooth; its internal texture is rough, and presents a fibrous appearance. Its specific gravity is

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* Annales de Chimie, tom. xi. p. 225.
Chemical System, vol. viii. p. 46.

nearly the same with water, being from 9.3335, to 10.000. It is inodorous, and is destitute of taste.

The physical property which eminently distinguishes it, is its high elasticity. It can be stretched to a great length, and when the force applied to it is withdrawn, it returns to its former dimensions. Its pliancy is increased by heat, while it is rendered more rigid by cold; and its softness, which is connected with the former quality, is so much increased by warmth, that it can be moulded into any form, and two parts newly cut may be pressed together, so as to be united. Mr Gough has remarked, that if caoutchouc be stretched, it does not easily recover its dimensions, if the temperature be diminished, but its elasticity is restored by moderate warmth *.

Caoutchouc, exposed to heat, softens, swells, and emits a fœtid odour similar to that of animal substances: as the heat is increased, it melts into a viscid matter, and remains in this state when cold. If heated sufficiently high, it takes fire, and burns with a vivid light, and dense smoke.

This substance is insoluble in water: it is softened when immersed in warm water; and in this state the fresh surfaces of two slips of it may be made by pressure to adhere together, an effect depending rather on the temperature, than on the agency of the water. Even when the water is boiled on it for a long time, it preserves its softness and elasticity, and suffers no apparent change.

It is also insoluble in alkohol: by boiling the alkohol upon it, it is deprived only of the carbonaceous matter which is interposed between each layer of it, as usually prepared: it is therefore by this operation rendered colourless, and the layers become more apparent.

Ether dissolves it. Macquer observed, that highly rectified sulphuric ether dissolves it readily; and by evapora-

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* Manchester Memoirs, New Series, vol. i. p. 288.

tion, the caoutchouc may be recovered unchanged. Berniard, on the contrary, found caoutchouc insoluble in sulphuric ether,—a difference of result, explained by a fact discovered by Cavallo, that ether is a proper solvent of this substance, only when it has been previously agitated with water; by which the small portions of alkohol and sulphurous acid which it often contains are removed. Pelletier has observed, that if caoutchouc be previously boiled in water, until it is swelled and softened, it is easily dissolved by the ether, and a very saturated solution is obtained *. Berniard, in the experiments which he published with regard to this substance †, states, that it is dissolved speedily in nitric ether, the liquid acquiring a fine yellow colour, even in the cold; and when heat was applied, the whole nearly of the caoutchouc was dissolved: but this can scarcely be considered as a proper solution, as it is rather owing to the decomposition of the caoutchouc, by the action of the nitric acid contained in the nitric ether; and he accordingly found, that when the solution was evaporated slowly, a substance was obtained of a yellow colour, transparent, friable, and soluble in alkohol, having therefore the characters of a resin, and which was not elastic.

Macquer found, that the volatile oils dissolve caoutchouc by the assistance of heat: these solutions are viscid, and when inspissated remain clammy. It is likewise dissolved by the fixed oils when they are boiled on it, and also by melted wax.

The alkalis, according to Berniard's experiments, do not dissolve caoutchouc in the cold: when macerated for six days in soapmaker's ley, it was not sensibly altered; but on boiling for half an hour, it was corroded.

The acids act upon it, and decompose it. In Berniard's

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* Mémoires de l'Institut. National, tom. i. p. 56.

† Journal de Physique, tom. xvii. p. 277.

experiment, sulphuric acid did not act immediately on caoutchouc immersed in it, but at the end of fifteen days the acid was coloured: it became black, and each fragment had the appearance of a piece of charcoal. Weak nitrous acid, digested in the cold on caoutchouc, produced in six days no sensible change, but at length corroded and hardened it, rendering it yellow: the strong fuming acid decomposed it quickly. Muriatic acid, either in the cold or with the assistance of heat, did not sensibly alter it: and even at the end of two months, the caoutchouc had preserved its colour, elasticity, and weight. Acetic acid, in the state of distilled vinegar, had no effect upon it *.

Caoutchouc, decomposed by heat in close vessels, afforded, in an experiment by Berniard, a watery liquid, and an empyreumatic oil, with ammonia: the elastic products he did not collect: there remained a quantity of charcoal. In this analysis, imperfect as it is, we perceive the approximation of this substance in composition to vegetable gluten. Fourcroy found too, that caoutchouc treated by nitric acid afforded nitrogen gas, with carbonic, prussic, and oxalic acids †.

This substance is applied to important purposes, from its softness and flexibility, its elasticity, its indestructibility, and not being affected by air, water, or the greater number of chemical agents. Tubes for conveying gases, and other chemical instruments, are prepared from it: and bougies, catheters, and similar surgical instruments of caoutchouc, are preferable to what can be prepared from any other substance. The difficulty in applying it to these uses, and which renders instruments prepared from it of a high price, is that of finding a solvent which can dissolve it, without alteration, so that by inspissation, it can be ob-

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* Journal de Physique, tom. xvii. p. 274.

† Annales de Chimie, tom. xi. p. 250.

tained with its properties unimpaired. The subject has engaged the attention of chemists, and different methods are at present employed.

Macquer having discovered the solubility of caoutchouc in ether, supposed that advantage might be taken of this, to apply it to these purposes; the concentrated solution being applied on a mould in layers, each layer being allowed to dry before another was laid over it. This method is too tedious and expensive to admit of being used.

The solutions of it in oils can scarcely be employed, as the inspissated caoutchouc remains clammy. Dr Roxburgh found, however, that the solution of it in what is named Cajeput oil, dried without any remaining clamminess; so that " a piece of catgut, covered with the half inspissated solution, and rolled between two smooth surfaces, acquired a polish and consistence proper for bougies *."

Grossart proposed a method in which the caoutchouc is not dissolved, but softened so far that it adheres †. A bottle of it is cut into a thin slip, and this is macerated in sulphuric ether until it is softened. It is then removed, and rolled spirally round a mould, pressing with the hand the sides of it closely together, and compressing the whole by a slip of tape and thread. A hollow tube is thus formed on the mould, and if this is made a little conical, it is easily withdrawn: or the removal is facilitated by plunging the whole in warm water, which softens and expands the caoutchouc. To lessen the expence, Grossart employed oil of lavender, or oil of turpentine, instead of ether, and found that either of them answered sufficiently well; a longer time only being requisite to have the tubes dry and firm. And in prosecuting these researches, he found that the same purpose was attained by warm water; which, proceeding in the same method as with the ether, softened the

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* Annales de Chimie, tom. xi. p. 143.

† Nicholson's Journal, 4to, vol. iii. p. 489.

slip of caoutchouc so completely, that its sides formed a perfect adhesion. The following directions have been given for the management of the process, the heat being best applied by the medium of boiling water: "Split a stick of cane, and then apply together again the split pieces, but with a slip of whalebone interposed between them. Cut the elastic gum into slips fit for twisting over the prepared cane, so as to cover it; then, by duly heating the surface of the cane covered with the caoutchouc, it will melt so as to form one piece. When cold, draw out the interposed whalebone from between the split cane; by which means, without difficulty, the whole substance of the cane may then be readily withdrawn from under the covering, thus leaving the tube formed as desired *." The surfaces to be joined should not be touched by the fingers.

The solution of caoutchouc in some of the oils, has been used as a varnish, to render flexible substances, as silk, &c. impermeable to water or air. It has the advantage of being flexible, but it is long before it dries, and it is liable to be softened by a very moderate heat. To render it less viscid, it is generally prepared from a mixture of volatile and expressed oil.

THE vegetable product known by the name of BIRDLIME, has a resemblance to caoutchouc, being like it possessed of tenacity and elasticity, and having nearly the same chemical properties; so much so, that they may perhaps be regarded as varieties of the same principle.

Birdlime appears to be a natural production, and exudes spontaneously from certain vegetables, forming a viscid matter, which collects on their leaves or stems. It is secreted in considerable quantity by the Robina viscosa. It

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* Philosophical Magazine, vol. xxii. p. 340.

is, however, generally extracted by an artificial process, which is, in some measure, kept secret. The following account of it is given by Geoffroy: "The inner bark of the holly is boiled in water seven or eight hours, till it become soft and tender. This is laid in masses in the earth, and covered with stones, placing one layer over another, the water having been previously drained from the bark. In this state it is left to ferment, during a fortnight or three weeks, in which time it changes to a kind of mucilage. It is then taken from the pit, pounded in mortars till reduced to a paste, washed in river water, and kneaded till freed from all extraneous matters. The paste is left in earthen vessels during four or five days, to ferment and purify itself. It is afterwards put into proper vessels, and thus becomes an article of commerce *." A similar substance is prepared from other vegetables; as from the wild vine, and the different species of misletoe: and, as remarked by Lagrange, the birdlime of commerce is often a composition of the above preparation with oil, turpentine, and other viscid substances. To obtain it pure, he prepared it from the inner bark of the holly, by a process nearly the same as that described by Geoffroy, and it is from his memoir † that the following account of its properties is principally taken.

It is of a greenish colour, and has a flavour somewhat acescent: its smell is similar to that of linseed oil: it is extremely viscid and tenacious; and when the hands are wet, so that it can be handled, it can be stretched out to a great length, and on withdrawing the stretching force, it gradually returns to its former dimensions. When stretched, its texture appears distinctly fibrous.

Spread on a glass plate, and exposed to the action of air and light, it dries slowly, becomes brown, and loses its

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* Nicholson's Journal, vol. xiii. p. 145.

† Ibid. vol. xiii. p. 144.

viscosity, so that, when quite dry, it can be reduced to powder; but it recovers it on the addition of water.

It reddens the infusion of litmus, from the presence of a little acetic acid, probably foreign to its composition.

When heated gently in a porcelain vessel, it melts, though without becoming very liquid: it acquires a brown colour; but on cooling, it recovers its characters. Placed on burning fuel, it burns with a bright flame, and the emission of much smoke; and it equally takes fire and burns when raised to a red heat in a crucible: a whitish residuum is obtained, which is very alkaline, and which also contains sulphate and muriate of potash, and carbonates of lime and alumina, with a small portion of iron.

Water has little action on birdlime. On boiling it in water, it does not dissolve, but acquires rather more fluidity, which it loses, however, on cooling; and the water receives merely a slight impregnation of acid and mucilage.

The action of the alkalis on it is energetic. Potash forms with it a whitish magma, ammonia being evolved. This matter is less viscid than birdlime: it hardens from exposure to the air, and its taste and smell are similar to those of soap: it is almost entirely soluble in water and in alkohol as soap is, and is decomposed by the acids.

The acids when diluted, soften and partly dissolve birdlime; when concentrated, they decompose it. Sulphuric acid blackens it, evolves charcoal, and causes a formation of acetic acid and ammonia. Nitric acid in the cold has little effect on it; but, on applying heat, the mixture becomes yellow, the birdlime dissolves, and as the evaporation advances, swells, leaving a hard brittle resinous mass. This, by being again subjected to the action of nitric acid, is converted into oxalic and malic acids. Muriatic acid in the cold has no action on birdlime: when heated on it, it turns it black. Oxymuriatic acid produces on it important changes, either by shaking the gas with the water containing birdlime, or by stirring it with the acid in a concentrated state: the birdlime loses its colour, and becomes white: it is no longer viscid, but in hard masses; and it is also no longer fusible. Acetous acid softens it, and dissolves a quantity, the liquor acquiring a yellow colour.

A number of the metallic oxides are reduced when heated with birdlime. Oxide of lead forms with it a compound of the consistence of plaster.

Alkohol, when boiling, dissolves birdlime: the solution, while hot, is transparent, but becomes turbid as it cools; and a yellow matter may be separated by filtration, which is softer than the original mass, melts in a moderate heat, and diffuses an odour similar to that of wax. The filtered liquor is bitter, nauseous, and acid; affording a precipitate on the addition of water, and leaving, on evaporation, a substance similar to resin.

Sulphuric ether is the proper solvent of birdlime: it dissolves it rapidly, and nearly entirely, leaving only impurities. The solution is of a greenish yellow colour, and reddens infusion of litmus. On adding water to it, the mixture thickens, and the ether swims on the top: if a sufficient quantity of water is added to dissolve the ether, a quantity of oil is formed on the surface, having an analogy to that of linseed. By evaporating the solution of birdlime in ether, a greasy substance is obtained, of a yellow colour, and of the consistence of wax.

Some chemists have supposed birdlime analogous to gluten; and there are certain points of resemblance between them. It differs from it, however, as Lagrange has remarked, in being less animalized; hence it is not liable to putrefaction, but can be preserved in water without any sensible change: it differs also in the great quantity of resinous matter that may be formed from it by nitric acid, and in its solubility in ether.

It is more analogous to caoutchouc, with which, however, it has not been usually connected. Like it, it is possessed of great tenacity and elasticity; is fusible, inflammable, affording much smoke at its combustion: it is insoluble in water, soluble in ether; and suffers changes somewhat similar from the acids, and even from the alkalis. It differs from caoutchouc, in being more easily acted on by these agents, in being soluble in alkohol, and in appearing to suffer rather more change in its constitution from these combinations. But these differences are not very considerable, and perhaps not greater than what may occur in varieties of the same species.

This conclusion receives confirmation from an observation made by Dr Roxburgh. The caoutchouc of the Ficus religiosus, the Ficus Indica, and the Artocarpus integrifolia, he found to be less elastic than that from the Hævea or the Urceola, but more viscid; while, in inflammability, and in their relations to the acids and other chemical agents, they are nearly the same. This fact, by proving that there are varieties of caoutchouc, not uniform in their properties, some of which appear to approach to birdlime, is sufficient, perhaps, to connect it with the species.

SECT. VIII.—OF WAX.

THIS substance, though apparently formed by the Bee, is a product of vegetation; it forms a kind of varnish on the leaves and stems of certain vegetables, or is mixed with their juices. Even that which is applied by the bee to the formation of its cell, has been supposed to be collected by that insect from flowers, and, in particular, from the pollen, or fine dust of the antheræ, which undergoes a slight elaboration in the body of the animal, so as to acquire that tenacity which fits it to the use to which it is applied. This opinion, however, as to the origin of bees-wax, has been refuted by the experiments of Huber. He has shewn, that bees form wax when they are denied all supply of the pollen of flowers, when they were confined to the hive, and supplied only with honey, or with sugar; and to obviate all fallacy, the comb previously formed was removed from the hive, and the bees were confined for such a period, as that no quantity of pollen, which they could have been supposed to have collected previous to their confinement, could have furnished the wax they formed. The honey or the sugar, too, always disappeared as the wax was formed; and, on the other hand, bees confined, and supplied only with fruits and the pollen of flowers, formed no wax. These facts appear to prove, that the pollen of plants is not the source of the wax which bees produce, but that it is formed from their saccharine food *.

Still wax is a vegetable product; and there are plants which afford it in nearly a pure state. Such is the plant named Myrica cerifera, or wax-tree, a native of Louisiana. Its seeds are encrusted with a white rough amylaceous like substance, which, when rubbed between the fingers, feels unctuous. When they are boiled in water, it is melted, and swims on the surface. This substance has been examined by Dr Bostock † and Mr Cadet ‡, and appears, from their experiments, to have nearly all the properties of bees-wax. Cadet has observed, that there are other species of myrica which afford a similar product; and that other plants, as the Croton sebiferum, the Tomex sebifera, the poplar, the alder, and the pine, yield by decoction an inflammable matter resembling wax. Besides these, a number of vegetables, natives of the torrid zone, yield varieties of wax in considerable quantity; and, according to Proust, the substance which forms the silvery like down on the leaves, flowers, and fruit of many plants, is an analogous product. It exists also, he affirms, in the fecula of

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* Nicholson's Journal, vol. ix. p. 182.

† Ibid. 8vo, vol. iv. p. 129. ‡ Ibid. p. 187.

certain plants, as in that of the house leek, or the green cabbage *.

Wax, taking the variety prepared by the bee as that best known, is a solid substance, brittle at a low temperature, but acquiring tenacity when slightly heated. It is tasteless, and nearly inodorous. Its colour is yellow; but this arises from the presence of some foreign matter, as it can be deprived of it, and be rendered white, without any change of its properties. The bleaching of wax, as this process is named, is performed by melting and running it into thin plates, which are exposed to the air, dew, and sun, until the colour is discharged.

Wax melts at a temperature of 142° of Fahrenheit †; and in cooling, passes through an intermediate state of softness to perfect solidity. It is incapable of being volatilized without change. It affords an elastic fluid when heated to ignition, consisting of its elements in a state of new combination; and this, when the air is admitted, burns with a clear and white flame. Hence the use to which wax is applied in affording artificial light. The products of its combustion are water and carbonic acid. When decomposed in close vessels, the products are a thick and empyreumatic oil in large quantity, a portion of water sensibly acid, carburetted hydrogen gas, analogous to olefiant gas, and a small portion of charcoal.

Wax is insoluble in water, and equally so in alkohol, at a low temperature. Dr Pearson found, however, that alkohol, by digestion on it at a temperature of 140°, dissolved it; and Dr Bostock found, that when alkohol is boiled on wax, it dissolves about a twentieth of its weight, the greater part of which is deposited as the solution cools. It is also dissolved by boiling ether, and the greater part dissolved by this fluid, is deposited as the temperature falls.

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* Nicholson's Journal, vol. v. p. 26.

† Ibid. 4to, vol. i. p. 70. &c. 8vo, vol. xvi. p. 105.

The action of the alkalis on wax is similar to that on the expressed oils, the combination taking place, however, more slowly, and only when the solution is boiled on the wax. Dr Bostock found, that a soap is thus formed, which is sparingly soluble in cold water, and which separates in flocculi as the liquid cools; in this the wax has lost its fusibility and inflammability; the compound is decomposed by the acids, the wax re-appearing with nearly its original properties. A compound of this kind with bees-wax forms the Punic wax of the ancients, which has been used as the basis of colours, and in encaustic painting. It consists of about one part of soda, with 20 of wax. Ammonia boiled on wax forms a white saponaceous compound, soluble in warm, but sparingly soluble in cold water. On vegetable wax, its action is more energetic than on bees-wax.

The acids act on wax with little force. Sulphuric acid, when its action is promoted by heat, is blackened by it, and at length dissolves it, forming a thick dark-coloured mass. According to the experiments of Beckman, wax boiled in diluted nitric acid is whitened and hardened. Oxymuriatic acid has been proposed to be used in bleaching it. Muriatic acid has little action on it.

It is dissolved readily by the fixed oils, when a moderate heat is applied, and forms a compound of an intermediate consistence, according to the proportions. Such compositions form ointments and cerates in pharmacy. It is dissolved by the volatile oils, with the assistance of heat.

From the properties now enumerated, it is evident that wax approaches nearly to the fixed oils. The principal difference is in its firmer consistence, and in its relation to some of the chemical agents, particularly to the alkalis. From the products of its combustion, Lavoisier inferred, that it consists of 82.26 of carbon, and 17.72 of hydrogen. The products of its decomposition by heat, shew that it also contains oxygen. According to its analysis by Gay Lussac and Thenard, its composition is carbon 81.784, oxygen 5.544, hydrogen 12.672.

The other varieties of wax have nearly the same properties. The wax of the Myrica cerifera, is somewhat different in colour and smell from bees-wax ; it is rather more fusible, melting at 109 ; it is somewhat more soluble in alkohol and ether ; and forms also a more soapy compound with the alkalis. Mr Brande submitted to chemical examination another variety of vegetable wax, brought from Brazil *. Its colour is greenish ; its smell agreeable ; it melts at 206 ; it is soluble in small quantity in boiling alkohol, and ether. It is not acted on by alkaline solutions, even when a boiling heat is applied ; a property in which it differs remarkably from the other varieties. The acids act on it in a similar manner ; and the results of its decomposition by heat are very similar to those of bees-wax.

The substance described by Dr Pearson under the name of White Lac, from India, appears similar to vegetable wax †. A similar product is obtained from common lac, in which it exists combined with resin, colouring matter, and a little gluten ; and is extracted by boiling in nitric acid, which dissolves the other principles, leaving the wax undissolved. And although this is an animal production, being the nidus of the Coccus or Chermes lacca, yet, as Mr Hatchet has remarked, it possesses few of the characters of animal substances ; and its properties, as well as its component ingredients, are such as belong to vegetable bodies ‡.

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* Philosophical Transactions, 1811.

† Ibid. 1794.

‡ Ibid. 1804.

SECT. IX.—OF FIXED OIL.

THE name of Oil is given to two vegetable proximate principles, which agree in the possession of unctuosity and a number of properties, but which likewise differ so far, that they must be regarded as essentially distinct. One of these species of oil is volatile at a high temperature; the other cannot be volatilized without decomposition; hence they may be distinguished by the epithets Volatile and Fixed. The volatile have been named Essential Oils,—the fixed, Expressed Oils, as it is by the process of expression that they are usually obtained. The chemical history of Expressed Oil is the subject of this section.

These oils are contained generally in the seeds and fruit of vegetables, and are found in largest quantity at or near to the period of maturity. They are extracted by expression; the fruit, or the seeds bruised, being subjected to pressure in a hempen bag inclosed in a press, and any foreign matter forced out with the oil being allowed to subside. In this way are prepared the oils from the fruit of the olive, and the seeds of the almond. The process is facilitated by the application of heat, or by previously roasting the seeds gently, especially with regard to those seeds which contain much mucilage: but from this the oil acquires acrimony and empyreuma; and is even so far changed in its qualities, as to be less liable to congeal, and more disposed to become dry or solid when exposed to the air. Oils prepared in this manner are hence named Drying Oils; and from these changes, the process is applied only to the extraction of the coarser oils, as those of linseed or rapeseed, or to oils required for particular purposes. Sometimes fixed oil is extracted by decoction, the seeds being bruised, and boiled in water, the oil separating, and swimming on the surface. In this way is prepared what is named Castor Oil, from the seeds of the Ricinus communis.

The oil which is extracted by either process has often an impregnation of foreign matter, whence it derives taste, flavour, and, in some cases, more active qualities. The oils of olives and of almonds are the purest, and appear to be free from any foreign impregnation. Oils less pure, but in larger quantity, are procured from linseed, hempseed, rapeseed, the nuts of the beech mast, and from the seeds of a number of other plants.

Fixed oils are fluid at moderate natural temperatures: by no great cold they are congealed, some of them even at a temperature not so low as the freezing point of water; and there are others, as the oil of the cocoa nut, of the laurel berry, or of the nutmeg, which are always concrete, whence they have obtained the name of Vegetable Butters. These peculiarities were considered as properties depending on the oil itself; but according to a view advanced by Braconnot, to be more fully stated under the history of animal fat, expressed oil, in common with all fatty substances, is not homogeneous, but composed of two principles, a fluid oil and a concrete substance, what he names pure fat or suet, somewhat analogous to spermaceti; and according to the proportions of these, the degree of consistence and fusibility will be various. They are separated by exposing the oil to a degree of cold sufficient to congeal it, and pressing the mass between folds of spongy paper. The fluid oil is imbibed, while the concrete fatty matter remains at length dry. Olive oil he thus found to consist of 72 of fluid oil, and 28 of solid fat: almond oil of 76 of the former, and 24 of the latter. This fluid oil does not congeal, but at much lower degrees of cold; and it is not liable to become rancid *. A similar view had been

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* { Annales de Chimie, tom. xciii. p. 225.
Philosophical Magazine, vol. xlvi. p. 55.

before given by Chevreul, with regard to animal fats; from which he had separated these two principles by the agency of alkohol, and by the action of an alkali, in the process of saponification. And he had observed, that in olive oil two different principles exist, and may be separated by congelation and absorption by bibulous paper. He has distinguished these principles by the names of Elaine and Stearine *. Their history falls to be considered under that of animal fat, with which they are more particularly associated.

Fixed oils are somewhat thick and viscid; when pure, they are transparent: they are colourless, or of a yellow or greenish tinge: they are insipid, or have a very mild taste. They are lighter than water. They are incapable of combining with water, as, even when strongly agitated with it, the globules of oil, when the agitation ceases, separate, and collect at the surface. They have been said to be insoluble in alkohol, but it has been observed, both by Bostock and Fremy, that they are dissolved in small quantity by that fluid †. One oil, Castor oil, is soluble in alkohol of the specific gravity of .820, in every proportion; in alkohol of a higher specific gravity, that of .840, it is stated by Mr Brande to be very sparingly soluble; the oils of almond and olive are very sparingly dissolved by alkohol of the former specific gravity; that of linseed is more soluble. Mr Brande farther found castor oil to be dissolved by sulphuric ether in every proportion, and almond, olive, and linseed oil, to be dissolved in considerable quantity ‡.

These oils cannot be volatilized without decomposition; and even this requires a high temperature. In general, they do not boil at a heat less than about 600° of Fahren-

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* Annales de Chimie, tom. xciv. p. 73.

† Nicholson's Journal, vol. xvi. p. 166. vol. xviii. p. 233.

‡ Philosophical Transactions. 1811.

heit; and when the operation is conducted in close vessels, so as to condense the vapour, the qualities of the oil are changed: it has lost its insipidity, has become acrid, and, by repeated distillations, is obtained more light and volatile, acquiring also an empyreumatic odour, and becoming soluble in alkohol. When this distillation is carried on with a strong heat, carburetted hydrogen, carbonic acid, and an acid liquor, are produced with the empyreumatic oil; and there is a residuum of charcoal.

Expressed oils are altered by exposure to the atmosphere, especially at a high natural temperature; they acquire a sharp taste, and a disagreeable smell, and become thick. This change is named Rancidity: it is owing to the absorption of oxygen which always accompanies it, as Berthollet long ago demonstrated *. The oxygen appears sometimes to combine with the entire oil; in other cases, to unite with part of its principles, and form an acid; there is also a portion of water slowly formed. When the oil is exposed to pure oxygen gas, the same change takes place more speedily; and some absorb a large quantity. Linseed oil, Saussure found, absorbed more than twelve times its volume of oxygen gas in the space of four months †, and this without forming any carbonic acid. Drying oils, or those extracted by expression with the assistance of heat, do not become rancid from exposure to the air, but, by the absorption of its oxygen, are converted into a resinous matter.

It appears that this absorption of oxygen by fixed oils may, under certain circumstances, be so rapid, as to evolve heat sufficient to cause them to burn. Many instances of spontaneous combustion had occurred from this cause, and, in particular, had been so frequent in the Russian arsenals, that at length a series of experiments was instituted, to as-

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* Mémoires de l'Acad. des Sciences, 1785, p. 529.

† Recherches sur la Vegetation, p. 154.

certain the circumstances connected with this. It appears from these, that if hemp, flax, or linen cloth, be steeped in linseed oil, if it lie in a heap, and be somewhat pressed together and confined, its temperature rises, a smoke issues from it, and at length it takes fire. The same thing happens with mixtures of oil with fine charcoal, as lamp-black wrapt up in linen. In one experiment, a mixture of this kind became warm in about sixteen hours, and emitted steam; in two hours more, it emitted smoke, and immediately took fire. In another, the combustion happened in nine hours. The experiment succeeded only when drying oils were used *. Charcoal alone, in some states, appears to be susceptible of spontaneous inflammation, when it is laid in heaps, or subjected to trituration, of which Sage has given examples †.

At the same temperature nearly at which oil is volatilized, it takes fire, and gives out a large quantity of light and heat. For this purpose, the oil must be converted into vapour, and its temperature raised to ignition. Hence is derived the utility of a wick in supporting its combustion; the wick drawing up a portion of the oil by capillary attraction: and by kindling the wick, the oil it contains being converted into vapour, and perhaps even decomposed or resolved into a variety of olefiant gas. Being ignited at the same time, it burns; and as fast as it is consumed, a new supply is afforded.

The combustion of oil is economically applied to obtain illumination, and with regard to this there are some facts of importance. Oil consists principally of carbon and hydrogen: the hydrogen requires rather a lower temperature for its combustion than the carbon does; hence the combustion of oil in atmospheric air is attended with a black

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* Journal de Physique, tom. xx. p. 1. 11. or Repertory of Arts, vol. iii. p. 95.

† Nicholson's Journal, vol. xxiii. p. 277.

smoke, which consists of the light carbonaceous matter suspended in the current of hot air. Where air has not sufficient access to the wick, this smoke is abundant; and it may, on the contrary, be entirely removed, by increasing the current of air, so as to render the combustion more rapid. This is done in Argand's lamp, which consists of a hollow wick, through the internal part of which a circulation of air is established; the combustion is thus rendered more rapid, and so much heat is extricated, and the air is so freely supplied, that all the carbon of the oil is consumed. Hence the combustion in these lamps is attended with no smoke; and from a given quantity of oil, more light and caloric are extricated, as the whole of that oil is consumed. It appears, however, that the full illumination is not obtained from the combustion of oil, under these circumstances, that might be expected. Hassenfratz, in a series of experiments, apparently performed with much care, and presenting some important results, on the light afforded by different combustibles *, found reason to doubt of the superiority of the lamp with an internal current of air, in the quantity of light afforded from the combustion of a given quantity of combustible matter, and even to conclude, that it is inferior in this respect (though superior in producing no smoke, and less smell) to a well-constructed lamp without this arrangement. The loss of light in the Argand's lamp giving rise to this unexpected difference, he ascribes to two causes: to part being absorbed by the glass chimney, and to the loss in the internal part of the hollow wick. The light which escapes from vapour in combustion, escapes from the external surface without interruption, but that from the internal surface is diminished considerably by passing through the flame. This Hassenfratz established, by causing the light from one burning body to pass through the flame of an-

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* Annales de Chimie, tom. xxiv. p. 78.

other. It is evident, that from this cause part of the light from the combustion of oil in a lamp with a hollow wick and internal current of air must be lost; and this loss must become greater from the rapid consumption of oil in the internal part of the flame. Accordingly, in a lamp with a double circular wick, the one within the other, the illumination is not so vivid as might be expected from the much greater consumption of oil. It follows from this, that there will be the least loss of light in an Argand's lamp, when the diameter of the circular wick is made small. And a lamp with a flat ribband wick, on the common construction, with a glass chimney placed over it, so as to admit of a current of air, and of rendering the flame steady and uniform, gives nearly as much light as an Argand's lamp.

The products of the combustion of oil are water and carbonic acid. Lavoisier found, that 100 parts of olive oil combine with 321 parts of oxygen, and produce 140 parts of water, and 281 of carbonic acid. Hence he inferred, that oil consists of 79 of carbon, and 21 of hydrogen. These must be regarded, however, only as approximations. That oxygen is also a constituent principle of oil, appears to be established by the production of carbonic acid and water in its decomposition, when transmitted through an ignited tube. The composition stated by Gay Lussac and Thenard, is carbon 77.213, oxygen 9.427, hydrogen 13.360.

The expressed oils suffer decomposition from the action of the greater number of the acids. Sulphuric acid renders them brown, and at length black, by evolving carbon in the state of charcoal: a portion of water is also formed. If heat be applied, the action is more rapid, sulphurous acid is evolved, and with certain proportions, the whole oxygen of the acid is abstracted, and sulphur obtained. Thenard has observed, that by the action of sulphuric acid on expressed oil in the cold, a compound is formed of a saponaceous nature, which, when washed with water, becomes white: it is acid, but less so, than if the acid it contains were uncombined; the oil, therefore, to a certain extent neutralizes the acid *. The action of nitric acid on oil is less violent; the oil is merely thickened and rendered white: when heat is applied, nitrous acid vapour is disengaged. The action is more rapid on the drying oils, a resinous-like matter being formed: and if heat be applied, the oil may even be inflamed by the acid. Muriatic acid has little effect on oil, when mixed with it in the cold; but according to Cornette, if the mixture is kept a long time in digestion in a sand heat, the colour darkens, and becomes black †. By distillation the acid passes over with little change.

With the alkalis, expressed oils form a chemical combination: the product is the well-known substance Soap. If one part of a pure expressed oil, as that of olives, be mixed with half its weight of the common potash ley, an imperfect combination is effected: the oil becomes thick and white, and the acrimony or causticity of the alkali is lessened. The compound is to a certain extent capable of combining with water: a perfect solution indeed does not take place, but an opaque milky mixture is formed, from which the oil does not separate completely. If heat be applied, the combination is rendered more perfect. To establish this, so as to form soap, one part of carbonate of soda is dissolved in 8 or 10 parts of water, and the carbonic acid is abstracted by lime: the liquor is filtered, and evaporated so far that its specific gravity shall be to that of water as 11 to 8. One part of this ley is mixed with two of an expressed oil, and the mixture is exposed to a moderate heat, sufficient to make the liquor simmer. It is agitated constantly, and the heat is continued till, on

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* Memoires d'Arcueil, tom. ii. p. 33.

† Mémoires de l'Acad. de Sciences, 1780, p. 565.

allowing a few drops of the liquor to fall on a stone, it congeals, and the water separates from it. It is then removed and cast in moulds.

This is the process for preparing the finer kind of soap. The coarser soaps are prepared from less pure materials; and the process which is followed, is somewhat different from that above described. An elaborate report was presented on this subject, by Pelletier, Darcet, and Lelievre*; and the account of the manufacture of soap which follows, is principally taken from their memoir.

The oily matter employed in the fabrication of common soap, is different in different countries. In France, the coarser kind of olive oil is used; and, according to the report of the French chemists, it forms the best soap. In this country, animal fat is employed; and, according to the same authority, it is, next to olive oil, that which gives the best hard soap. The alkali which answers best, is soda: it forms a soap which easily becomes concrete, while potash forms one that remains soft. In countries, therefore, where barilla can be obtained at a low price, it is used. In this country it would be too expensive: the potash of commerce is employed: and in order to render the soap sufficiently disposed to congeal and become hard, there is added, towards the end of the boiling of the alkaline ley with the unctuous matter, a quantity of sea salt; the soda of which, being in part evolved by the potash, produces this effect.

The alkali must be in its pure, or caustic state: whether barilla or potash, therefore, be employed, the carbonic acid is abstracted by lime, and the solution thus obtained forms the soapmakers' ley. When barilla is employed, after being reduced to coarse powder, it is mixed with the lime: the proportions used being 5 lbs. of barilla with 1 of lime. The mixture is put into a large wooden trough, with such a quantity of water as will cover it several inches: it is stirred; and after it has stood some hours, the ley is withdrawn, and is named the first ley: it is of such a specific gravity, that a fresh egg does not sink in it. A new quantity of water is poured on the materials, and after some hours, is drawn off, affording a weaker ley. This is repeated once more, forming a third ley: and lastly, the residuum is washed with water, which now receives so slight an impregnation, that it is reserved only for adding to a fresh quantity of the materials.

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* { Memoires de Chimie de Pelletier, tom. ii. p. 249.
Annales de Chimie, tom. xix. p. 253.

The proportion of oil that is requisite is 6 parts, when 5 of barilla and 1 of lime have been used. To combine them, they are to be boiled together: the boiler is a large iron pot fixed in a brick furnace, there being adapted to it a crib of wood: the oil is put into this boiler, with a portion of the weakest or third ley, and heat is applied, so as to cause the mixture to boil: fresh portions of the ley are added, until the whole is consumed: the second or stronger ley is added in the same manner; the mixture being well stirred: the oil unites with the ley; and after some hours of boiling, the mixture becomes uniform, and acquires a thick consistence. A small portion of the first ley is then added; the successive addition of small portions is continued; the mixture becomes more and more thick, and the soap now formed begins to separate from the watery liquor; a small quantity of sea salt is then added, which renders the separation more complete, by attracting the water: the boiling is continued for two hours longer, the fire is then withdrawn, and the whole is allowed to remain at rest. In a few hours the soapy matter collects towards the surface, and the watery part subsides: this last is drawn off by a tube at the bottom of the boiler: the fire is then again applied, a small quantity of water or of weak ley being added, to facilitate the liquefaction of the soap. The mixture being liquefied, and being brought to ebullition, the remaining part of the strong ley is added in small quantities. The congelation of the soap can now be discovered; the degree of which is judged of, by withdrawing a small portion, and allowing it to cool on a plate of glass. If it be sufficiently firm, the fire is withdrawn; the soap is left at rest for some hours; the liquid beneath is withdrawn by the stop-cock: the fire is again applied, a small quantity of water being added to promote the liquefaction; and when the whole has cooled a little, it is run into the vessels in which it is to congeal, in the bottom of which a little lime in powder is strewed. After some days, the soap has become sufficiently firm to be cut into the form under which it is sold.

Though such be the general outline, it is no doubt varied by different manufacturers, and in different countries; but by following this process, a soap of excellent quality may be formed. In this country, the principal difference is in using animal fat, to which, in forming yellow soap, a portion of resin is added; and frequently potash is used instead of soda: in this case it is necessary to use muriate of soda in larger quantity than when barilla is employed, in order to afford a portion of soda, to render the soap concrete. The French chemists, in their experiments on soap, found, that when they substituted a ley from potash for that from barilla, they obtained only a soft soap. But if they added in the course of the boiling a solution of muriate of soda, they obtained a soap perfectly firm: or if they began the process with a ley of potash, and finished it with a ley of soda, they had the same result: our manufacturers use in general a portion of the ley from kelp. The process, as it is conducted in this country, is described in Aikin's Chemical Dictionary, under the article Soap. The following are given as the materials and the proportions, from which a good yellow soap is prepared: 25 cwt. of tallow, 4½ of oil, 7 of resin, 18 of barilla, and 10 of what are named black ashes, being the saline residuum of the waste ley recovered by evaporation, and calcined. There is sometimes added to the whole a little palm oil. The produce is about 64 cwt. of soap.

The veined or marbled soap differs from the other in its streaks of colour, and in being prepared from the purest materials, as it is used for medicinal purposes. The variegated colour is given to it, by adding to the soap, when nearly fully boiled, a small quantity of fresh alkaline ley, and soon after a solution of sulphate of iron ; black oxide of iron is thus precipitated, which, from the action of the soap, assumes a blue tinge. Brown or red oxide of iron is then diffused in water, and stirred through the soap, so as to be mixed with it in streaks.

The soft soap of commerce is prepared from the common potash, rendered caustic by lime, and boiled with some of the coarser oils, as rapeseed, hempseed, or linseed, or even with fish oil.

Soap is frequently adulterated. The most common method is to cause it to imbibe a large quantity of water ; and to prevent the dissipation of this from exposure, those who practise it keep the soap in a saturated solution of muriate of soda. This is detected by the great loss of weight which such soap sustains from exposure to the air. Other modes are also said to be practised, as by the addition of chalk, clay, alum, sea salt, and other substances.

Pelletier and Darcet executed the analysis of soap. When properly prepared, 3 lbs. of oil ought to furnish 5 lbs. of soap : but from this it is not easy to discover, with perfect accuracy, what proportion of alkali and of water it contains. The proportions they assign are, in 1 lb. of soap, 9 ounces 6 drachms of oil, 1 ounce 3 drachms of pure alkali, and 4 ounces 7 drachms of water.

The cleansing property of soap depends on the alkali it contains : the alkaline power is no doubt impaired by the combination ; and it might be supposed more economical, to use the alkaline solution. In some cases it is so, as in the process of bleaching; but for common use, soap has some advantages; as it acts less on the fibre of the cloth, and gives it a softness and smoothness, which the alkali alone would not do.

Soap is soluble in water; but the solution is milky. It is also soluble in alkohol; and if the purest soap has been employed, this solution is nearly transparent; if strong, it is of a gelatinous consistence.

Soap is decomposed by the acids, which attract its alkali, and separate its oil. The greater number of the salts also, either earthy or metallic, effect in it the same decomposition. This is the reason that, with what are termed Hard waters, a proper solution of soap cannot be formed, —the sulphate of lime contained in the water decomposing the soap. In the decomposition of soap by the earthy and metallic salts, the oil combines with the earth or metallic oxide. When this oil is separated by an acid from the soap, its properties are altered; and, in particular, it is soluble in alkohol. During its conversion into soap, therefore, it must have undergone some chemical change. It has been supposed to receive oxygen from the air; and this seems to be confirmed by the experiments of Fremy *, but is denied by Chevreul.

A peculiar product was obtained by Chevreul from the decomposition of soap, what he named Margarine. On leaving soap immersed in water, one part of it is dissolved, while another part is precipitated. On washing this with alkohol, and submitting it to the action of muriatic acid, which combines with the alkaline base, the margarine is separated in pearly scales. As a product more peculiarly of animal fat, and as connected with the other principles, stearine and elaine, obtained by the same chemist, it is afterwards to be considered under their history. Chevreul has supposed it to be of the nature of an acid; and hence

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* Nicholson's Journal, vol. xviii. p. 251.

to exist combined with the alkali of soap, somewhat in the manner of a saline compound. He also found another product of an acid nature, what he names Oleic acid, in a similar state of combination; and the process of saponification seems to consist in the formation of these two products from the fatty or oily matter, or rather from the stearine and elaine of the fat, and their combination with the alkaline base,—the Sweet Principle, as it is named, of oils being a product which is at the same time separated *. A similar view has been given by Braconnot. The action of the alkali in the formation of soap, he supposes to consist in its converting the oil or fat into two products, an oily matter, and a concrete fat similar to what is called Adipocire; this latter being analogous to the Margarine, the former to the Elaine of Chevreul, and with these the alkali combines. He gives the following as the composition of the soap of olive oil, water 21.36, adipocire or concrete fat 9.20, oily matter soluble in alkohol 59.20, soda 10.24 †.

Ammonia forms with the expressed oils a saponaceous compound, which is thick and white, and which is diffusible in water. The combination, however, is less intimate than that with the other alkalis, as heat cannot be applied to render it perfect. Berthollet obtained a proper ammoniacal soap, by the indirect process of mixing a solution of common soap with a solution of muriate of ammonia: the muriatic acid is attracted by the alkali of the soap, and the oil combines with the ammonia, forming a kind of coagulum. This soap is less soluble in water than common soap, has a more pungent taste, is less consistent, and is decomposed by long exposure to the air. It is soluble in alkohol.

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* Annales de Chimie, tom. xciv. and xcv. Annals of Philosophy, vol. vii.

† Annales de Chimie, tom. xciii. p. 268. Philosophical Magazine, vol. xlvi. p. 135.

Berthollet, in a memoir on the combinations of oils with earths and metallic oxides *, has described the properties of the saponaceous compounds thus formed.

Lime-water acts upon expressed oil nearly in the same manner as an alkaline solution, forming a white and thick mixture; but the proper calcareous soap he found to be formed by mixing a solution of soap with a solution of sulphate, muriate, or nitrate of lime, or by adding it to lime-water; the lime unites with the oil of the soap, and forms a combination sparingly soluble, which remains on the filtre. By a similar process, he formed magnesian and argillaceous soaps,—adding, to form the one, a solution of sulphate of magnesia, to form the other, a solution of alum, to a solution of common soap. The magnesian soap was of the utmost whiteness, unctuous, dried with difficulty, and preserved its white colour after exsiccation. It melts with a moderate heat, and forms a transparent mass, slightly yellow, and very brittle: it is insoluble in boiling water, but alkohol dissolves it; when water is added to the solution, it becomes milky. The argillaceous soap was soft and tenacious, and preserved its tenacity in drying; it melts readily, and exhibits, after fusion, a mass of a beautiful transparency, rather yellow. It appeared to be insoluble in water, alkohol, or oil. The solution of muriate of barytes afforded, with soap, a combination nearly the same in appearance and properties, as the soap of lime.

Combinations of expressed oil with metallic oxides can be formed by a similar process,—adding to a solution of soap a solution of a metallic salt: and the properties of a number of these compounds were examined by Berthollet. The combination with oxide of mercury, he found to be viscid; to dry with difficulty, losing its white colour in drying; to be soluble in oil, and very sparingly in alkohol:

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* Memoires de l'Acad. des Sciences, 1780, p. 1.
Nicholson's Journal, 4to, vol. i. p. 170.

that with silver is at first white; but after a few moments' exposure to the air, it becomes red: that of gold, which is also at first white, soon assumes a purple colour; these changes of colour being probably owing to the facility with which their respective metals part with oxygen. The combination with oxide of iron is of a reddish-brown colour, tenacious, and easily fusible; that with copper is of a green colour: when digested in alkohol, its colour becomes deeper, and it liquefies, but does not dissolve in the cold: ether renders its colour deeper and more beautiful, and dissolves a considerable quantity of it: it is also soluble in oils, to which it gives a fine green tinge. This, on account of its solidity and its fine green colour, has been proposed to be used as a paint [*]. The compound with oxide of lead is white, tenacious, and adhesive when heated: that of tin is also white: it is not, like the other metallic soaps, fusible; but is decomposed by heat. The soap of zinc is yellowish white, dries speedily, and becomes friable: that of cobalt is of a dull leaden colour, and dries with difficulty; and that of manganese white, but, on exposure to the air, assumes a peach-bloom colour, which gradually deepens [†].

Expressed oil is capable of acting on some of the metallic oxides, and even of promoting the oxidation of some of the metals. If copper be rubbed with grease, and exposed to the air, the surface becomes green, the fat absorbing oxygen, which acts on the metal. The oxidation of mercury by trituration with lard probably depends on the same agency. With oxide of lead, expressed oil combines, either by trituration, or in a more perfect manner by boiling; and by the last method, so much of the oxide is dissolved, that the compound, when cold, assumes a solid consistence. This forms what in pharmacy is named Common Plaster, prepared by boiling two parts of oil with one of vitrified oxide of lead *(litharge)*, adding a small portion of water to prevent the composition from being scorched. Its texture is foliated, and it is easily melted. From its adhesive quality and its mildness, it is well adapted to the uses to which it is applied in surgery. Deyeux, who has made some observations on these combinations *, has remarked, that some other metallic oxides, as those of bismuth and mercury, may be made to afford similar compositions with oil. In the action of expressed oils on litharge, Scheele observed, that a substance of a sweet taste is produced, which remains dissolved in the water with which the litharge and oil are boiled. During this action, it appears, carbonic acid and water are formed, and this leaving oxygen redundant gives rise to the formation of the Sweet Principle, which resembles sugar in several of its properties, but differs from it in others, particularly in being volatile, and in not being capable of fermenting. The oil also becomes volatile and soluble in alkohol †.

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[*] Journal de l'Ecole Polytechnique, Cah. iii. p. 427.

[†] Nicholson's Journal, 4to, vol. i. p. 172.

Expressed oil combines with sulphur, by boiling them together. This solution, named Balsam of Sulphur, has a reddish-brown colour, a fœtid smell, and acrid taste. When heated, it emits sulphuretted hydrogen. When concentrated, sulphur is deposited from it, crystallized in octaedrons.

Expressed oil dissolves phosphorus with the assistance of heat. The liquid is luminous when exposed to the air. When saturated, a part of the phosphorus is deposited, on cooling, in octaedral crystals.

It unites with several of the vegetable products; gum, fecula, and sugar. If triturated with any of these, and a little water, it forms a milky fluid, from which the oil does not immediately separate. Mucilage suspends it more completely than either of the others; and is frequently used in pharmacy for this purpose.

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* Annales de Chimie, tom. xxxiii. p. 50.

† Nicholson's Journal, vol. xviii. p. 251.

Expressed oils are applied to many purposes in the arts. They form the basis of paints, the oil being triturated with white oxide of lead, and the colouring matter being afterwards added. Combined with resin and turpentine, they form Fat Varnishes, which differ from the spirit varnishes in being more flexible. Mixed with lamp-black, they form the composition used as printing-ink. For these uses, the drying oils, those of linseed, poppy, hemp, or nuts, are employed; and they require even preparation. Not only is the seed from which they are extracted previously roasted, but the oil is strongly boiled for some time, is even sometimes kindled, and allowed to burn for a little; or is boiled with a little litharge. By these processes the qualities of the oil are materially modified, and, in particular, the unctuosity is lessened, as is apparent in the facility with which printing-ink is impressed on paper, without spreading or giving a greasy stain.

It is under the form of drying oils that oil is used as the vehicle of colour in painting, the colours being mixed with the oil; and there is a considerable degree of nicety with regard to their preparation. It appears, that a portion of the mucilaginous matter, originally contained in the oil when it had been expressed, adheres to it; this prevents the oil from flowing so smoothly from the pencil, and the composition dries slowly and unequally, not by inspissation of the whole layer of the oil, but by thin pellicles forming successively, whence false shades are communicated. Various additions have been made to remedy these inconveniences; such as litharge, or other salts of lead, and some saline substances. But the risk in employing these is, that the colours are more or less injured by them; and as this injury may in some cases take place very slowly, it is difficult to make the experiment, so as to ascertain what additions are harmless, and what may ultimately prove injurious. It is therefore still a desideratum to have a process to prepare these oils for the finer kinds of painting.

It has been often the practice to use not the drying oil alone, but a solution of amber or copal, in the oil, to mix up the colours, this drying more quickly and equally; and it has been supposed, that this was employed as a vehicle of colours by some of the older painters, especially those of the Venetian school. This, however, is doubtful, and it has been affirmed, that when either copal or amber is used, the composition dries too quickly, dries hard, and is therefore liable to scale. It is the practice, it is said, of many artists, to use a composition of mastich, which is not liable to these inconveniencies. It consists of equal parts of a solution of mastich in turpentine, and drying linseed oil, with which the colours are mixed.

SECT. X.—OF VOLATILE OR ESSENTIAL OIL.

THE volatile, though agreeing with the fixed oils in unctuosity, inflammability, and several properties, differ from them in others. They are volatile at a low temperature, and may be distilled by the heat of boiling water, without being decomposed; they are soluble in a small proportion in water: they are more soluble in alkohol, and they do not easily combine with the alkalis. They are in general odoriferous, pungent, and acrid; and are more highly inflammable than the fixed oils.

These oils exist principally in the aromatic plants. In some plants the oil is confined to the flowers, the fruit, the leaves, or bark; sometimes it is contained in several of these parts, and in a few instances it is diffused through every part of the plant. The quantity varies, not only according to the age, but according to the vigour of the plant, hence it is dependent on climate, soil, and season.

It is remarkable, that though in general the odour resides in the essential oil, there are some odoriferous flowers, as the violet or jessamine, which yield little, if any, yet they lose their flavour by a gentle heat.

Some of the essential oils being contained in distinct vesicles, may be obtained by pressure. In this manner, essential oils are obtained from lemon and orange peel. Usually they are obtained by distillation; the vegetable substance being submitted to heat, with a considerable portion of water, in the common still. The heat of boiling water is sufficient to volatilize the oil: it is therefore carried over with the aqueous vapour: the water when it is condensed retains the taste and flavour of the plant, from having dissolved a small part of the oil; the greater part, however, separates, and swims on the surface, or sinks to the bottom. The oils prepared in this way are named Distilled Oils; and the waters impregnated with them, Distilled Waters.

The essential oils are in general lighter than water; though a few produced from aromatic plants, as cloves or cinnamon, are heavier: they are thin and fluid; sometimes viscid: some congeal at a moderate reduction of temperature, others remain fluid at intense colds. In congealing they assume a crystalline arrangement. A few oils are obtained concrete, such as that of roses. Their colours are various, and each has a peculiar odour and taste; the odour is that of the vegetable from which it is extracted.

The essential oils are volatilized by a very moderate heat: if a greater heat is applied to them, they suffer a change in composition and properties; hydrogen is evolved, and charcoal is obtained as a residuum.

These oils exposed to the air, gradually lose part of their smell; are thickened; and at length become nearly concrete: depositing crystals of an acid nature. These changes are owing to the absorption of oxygen, which oxidizes a portion of the oil, so as to form an acid similar to the benzoic; while the greater part, either by the loss of part of its hydrogen, or partly from this, and partly from the fixation of oxygen, is converted into a substance of a resinous nature. From some, too, there is a deposition of camphor. Braconnot has supposed, that the essential oils, like the expressed oils, are not altogether homogeneous, but contain along with a fluid oil, a portion of concrete matter, which in general is analogous to camphor, so that this principle bears to these oils the same relation that suet does to the fat oils. In others of them, those in particular which are concrete, as the oil of roses, or those which congeal at very moderate colds, as the oil of anise or fennel, the concrete matter seems to be of a different kind.

The volatile oils are inflamed more easily than the fixed are, and their combustion is more rapid. The products of the combustion are water and carbonic acid. They yield more water than the fixed oils do; hence they appear to differ from the fixed oils, in containing more hydrogen proportioned to their carbon.

The essential oils are dissolved by water, but in small quantity, only as much as communicates flavour and taste. Distillation is not necessary to this combination, mere agitation is sufficient; and thus waters may be formed, as strongly impregnated as those which are distilled.

The essential oils are more soluble in alkohol. Some combine with the alkohol in every proportion, others in limited quantities; and there are some which are sparingly soluble, as oil of lemon peel or of turpentine,—affording in common, with many facts relating to the chemical relations of the vegetable principles, a proof that in each the properties are not perfectly uniform, but exhibit gradations, undoubtedly from slight variations in the composition which constitutes the species.

The action of the acids on the essential oils, is more violent than on the fixed oils. Sulphuric acid blackens them instantly, and sulphurous acid and carbonic acid gases are disengaged with considerable heat. Nitrous acid acts so powerfully, as often to inflame the oil; and the inflammation almost always takes place when a little sulphuric acid is mixed with the nitrous acid. If the nitric acid be added more slowly, and with precaution to guard against inflammation, it appears from an experiment by Chaussier *, that prussic, malic, and oxalic acids are formed; the remaining oil is converted into a viscous resinous substance, and much carbonic acid, nitric oxide, and nitrogen gases, are evolved during the operation. The action of muriatic acid is less violent; it deepens the colour of the oil, and thickens it. The oxymuriatic converts these oils into a resinous-like matter.

In some cases the essential oils appear to combine with acids, instead of being decomposed; and the acid, as Thenard has remarked, is neutralized by the oil, so that its existence is not obvious in the compound from any sensible acidity. The substance produced by the action of muriatic acid on oil of turpentine, which has been named Artificial Camphor, he regards as a compound of this nature.

The essential oils combine with difficulty with the fixed alkalis. By long trituration a combination is effected, and a saponaceous compound is formed; which is much less perfect, however, than that formed by the fixed oils with the alkalis. From the observations of Pelletier, it appears, that when the alkali is saturated with carbonic acid, it combines more easily and perfectly with the essential oils, than when it is pure: and he has supposed, that the indirect processes employed by chemists to form these combinations, succeeded in consequence of the absorption of

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* Journal de l'Ecole Polytechnique, Cah. iv. p. 674.

carbonic acid from the atmosphere *. Others have supposed the effect to depend on the absorption of oxygen.

Liquid ammonia, distilled with the essential oils, dissolves them, but sparingly. It combines readily, however, with them when they are dissolved in alkohol.

These oils dissolve sulphur. The solution has an offensive smell and taste. When saturated, it deposites part of the sulphur in transparent crystals. They likewise dissolve phosphorus; and from this saturated solution the phosphorus is deposited in a crystalline form. The addition of a portion of camphor causes it to remain dissolved. Some of these solutions, such as that in oil of cloves, are luminous, without much heat.

They decompose some of the metallic salts, first attracting the oxide, from which the oxygen continues to be slowly attracted, probably by the hydrogen of the oil, so that the metal is at length precipitated in its pure form.

The volatile oils unite in some measure with mucilage or with sugar; and by the medium of either of these they may be suspended in water.

They are in general used as perfumes, or in the practice of medicine. Some of them enter into the composition of varnishes.

These oils are frequently adulterated, either by the addition of some cheaper essential oil, as that of turpentine, of a pure fixed oil, as oil of almonds, or of alkohol. The first is betrayed by its smell, when a little of the adulterated oil dropt on paper is heated before a fire; the second by the oil dropt on paper leaving a greasy stain, after the paper has been exposed to as high a heat as it can bear, and by not being soluble in alkohol; the third by becoming milky when it is mixed with water.

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* Mémoires de Chimie, tom. i. p. 328.

SECT. XI.—OF CAMPHOR.

CAMPHOR in many of its properties resembles the volatile oils: it is odorous, pungent, volatile, inflammable, sparingly soluble in water, and abundantly soluble in alkohol. It differs from them principally in its concrete form, its relation to the acids and alkalis, and the results of its decomposition by heat.

Camphor is a principle contained in many vegetables, especially the aromatic plants: it appears to be volatilized in combination with their essential oil in the process of distillation, and, when these are long kept, is deposited in a crystalline form. Proust extracted it in this way from oil of lavender, of sage, and other labiated plants; the first, by spontaneous evaporation, affording one-fourth; the second one-eighth of its weight. The process he followed, was to distil oil of lavender with the heat of a water-bath inferior to 212°, until one-third had passed over; the remaining quantity when cold affords camphor, which may be separated from the adhering oil by pressure between folds of bibulous paper; when refined by sublimation with a little lime, it is similar to common camphor, but retains somewhat of the odour of the essential oil*. Peppermint, rosemary, and other plants of this country, also afford it.

The Camphor of commerce is procured from the Laurus camphora, a native of the east of Asia. It exists in the wood of this tree in vesicles, and when picked out, forms what has been named Native Camphor. It is usually procured by the process of sublimation. The wood of the stem and branches, cut into small billets, is exposed with a little water to a moderate heat, in a kind of alembic, to the head of which is adapted a capital in which straw is put. The camphor is volatilized, and attaches itself to the straw. It is purified in Europe by a second sublimation.

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* Annales de Chimie, tom. iv. p. 179.

The camphor of commerce, from its mode of preparation, is in the form of semi-spherical cakes: it has a texture somewhat striated, with a degree of ductility, in consequence of which it can be compressed, and is not easily reduced to powder; is of a white colour, and semi-transparent; a little unctuous to the feel; has a strong, peculiar, and rather a fragrant odour, and a taste which is pungent and bitter. It is susceptible of crystallization when slowly sublimed; when slowly precipitated from its solution in alkohol by the affusion of water, in appears in the form of acicular prisms.

Camphor is even more volatile than the essential oils. It evaporates at the common temperature of the atmosphere, losing weight, and an angular fragment becoming spherical; at a temperature between 100 and 150, it sublimes in close vessels unchanged. If heated under compression, or if suddenly heated under the pressure of the atmosphere, it becomes fluid before it passes into vapour; and in the process of subliming it in the large way, the heat is so applied, that the camphor is rendered fluid, and the sublimed cake is thus obtained more dense. The temperature at which it melts is, according to Venturi, 302° of Fahrenheit.

It is highly inflammable, kindles very readily, and burns with the emission of much light, and with a dense black smoke, which condenses into a smooth light charcoal. Carbonic acid gas is produced, and a portion of the peculiar acid which has been named Camphoric Acid.

Camphor is sparingly soluble in water. When triturated with it, it communicates smell and taste to the water, which remains odorous, and somewhat pungent; but scarcely any appreciable quantity is dissolved. A phenomenon which has excited some attention is presented, when pieces of camphor are placed on the surface of pure water. They begin to move with rapidity, and while moving dissolve, the solution taking place at the line where the water and the air are in contact, so that a cylinder of camphor immersed in water part of its length, becomes excavated, and at length is cut through, exactly on a level with the surface of the water. The motions of the camphor are, according to Venturi, owing to this cause; the rotation of the small pieces at the surface being the mechanical effect of the re-action which the oily liquor, (into which the camphor, by the solvent power of the air and water, is resolved), extending itself upon the water, exercises against the camphor itself*.

Camphor is soluble in alkohol: the solution is decomposed, and the camphor precipitated in a white powder, by the affusion of water; if the water be slowly added, and merely in such a quantity as to weaken the affinity of the alkohol to the camphor, the latter, in separating, presents a dendritic crystallization. It is also soluble in expressed and essential oils, and from these solutions, when saturated, the camphor separates in a crystalline form.

The alkalis do not act on camphor. Of the earths, magnesia appears to exert some action on it, as, when they are triturated together, the camphor is reduced to a smooth impalpable powder, which is easily diffused in water.

The action of the stronger acids on camphor is peculiar, and presents some singular results.

Sulphuric acid digested on it renders it brown; and a brown or reddish solution is obtained, from which, on the addition of water, camphor is precipitated. This takes place, however, only at a certain stage of the process; and Mr Hatchet, in his experiments on artificial tannin, investigated other changes which happen. Camphor added to concentrated sulphuric acid, gradually dissolved, forming a solution which, from a yellow, deepens to a blackish brown, sulphurous acid gas being disengaged: at the end of two days this ceases: but on placing the vessel on a sand-bath, it renewed. After two days more, on adding water, a coagulum of a reddish brown colour is formed; and the odour of sulphurous acid is succeeded by one resembling that of a mixture of oils of lavender and peppermint. The whole being distilled, the water impregnated with this odour passes over, accompanied by a little of a yellowish oil; there is then a slight production of sulphurous acid gas: water being added, and the distillation continued until a dry blackish brown mass remains; by the action of alkohol, part of this is dissolved, part remains undissolved: the latter has the appearance of a compact coal: the dissolved matter has the properties of tannin *. Chevreul observed the same products nearly, from the action of sulphuric acid on camphor; the coally residuum he regards as a compound of carbon highly hydrogenated with sulphuric acid; the soluble astringent matter he considers as a similar compound with a larger proportion of acid, and having the carbon combined with a still larger proportion of hydrogen. And the sulphuric acid is so intimately combined in these products, that it is not abstracted by barytes †.

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* Nicholson's Journal, vol. i. p. 207.

The action of nitric acid on camphor is very different. In the cold it dissolves it, and the solution divides into two portions,—a yellowish liquid of an oily-like appearance, and a watery liquor which collects beneath. The first contains camphor in solution in nitric acid, and is decomposed by the affusion of water: not more than two-thirds of the camphor operated on, however, is recovered: the remain-

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* Philosophical Transactions, 1805.

† Philosophical Magazine, vol. xxxvii. p. 425.

ing quantity appears to exist in the state of an acid, with nitric acid in the watery liquid. By the greater number of the other acids camphor is dissolved. Muriatic acid gas and fluoric acid gas dissolve it, and form a combination which is decomposed by water; liquid muriatic acid, as well as acetic acid, effect its solution; and Bergius found, that water impregnated with carbonic acid dissolves a larger portion of it than pure water *.

By distilling nitric acid from camphor, it is converted into a peculiar acid, which has received the name of Camphoric acid. The process consists in distilling from 4 ounces of camphor in a retort, 1 lb. of nitric acid, so far diluted as to be of the specific gravity of 1.33, the heat being gradually applied by a sand-bath: nitric oxide and carbonic acid gases are disengaged; part of the camphor rises in vapour, while the other part receives oxygen from the acid. When the vapours have ceased, the camphor condensed in the receiver is returned into the retort, another pound of acid is added, and the distillation is renewed. This is repeated, until all the camphor is acidified. According to Lagrange, about 5 pounds of nitric acid are required to acidify 4 ounces of camphor †. The camphoric acid crystallizes in the remaining liquid. The crystals being placed on a filtre, are washed with distilled water, to carry off any nitric acid. They amount to nearly half the weight of the camphor.

Camphor may be decomposed by heat: and the experiment is instructive, as pointing out the nature of this principle. Some management is requisite to submit it to a heat sufficiently high, and yet prevent its volatilization. The process followed, is to mix it with pure clay: six parts of clay being taken to one of camphor: both are reduced to powder, and intimately mixed: and the mixture is made

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* Materia Medica, p. 520.

† Nicholson's Journal, 4to, vol. ii. p. 157.

into a paste with water, which is made into small balls, and well dried. These are heated in a retort connected with a receiver containing distilled water. Part of the camphor is sublimed, but the greater part is decomposed; an oily fluid distils over, which swims on the surface of the water; a portion of camphoric acid is produced, which the water dissolves, and there remains in the retort a quantity of charcoal mixed with the clay; there are also disengaged carburetted hydrogen, and carbonic acid gases. Four ounces of carbon yield, according to Lagrange, 12 drachms of oil, and 8 drachms of charcoal, besides the camphoric acid and aërial fluids *.

The oil of camphor, as this product of the decomposition has been named, is of a golden yellow colour; has an aromatic odour, and an acrid burning taste, leaving a sense of coolness on the tongue. It is volatile: when exposed to the air it evaporates partially, and there remains a thick yellow matter, which at length also evaporates. It is volatilized by heat, and is inflammable. Alkohol dissolves it, and the solution is rendered milky, on the affusion of water. It combines with the alkalis, affording a compound soluble in water, and which has the characters of the soap made with volatile oils.

This substance has evidently the properties of a volatile oil; and hence its production from the decomposition of the camphor, points out the chemical constitution of this principle. As it is resolved into this oil and into charcoal, or compounds containing carbon, it is obvious, that it differs from the volatile oils principally in the larger quantity of carbon which enters into its composition.

It has already been stated, under the history of the compounds of carbon and hydrogen, that the vapour of camphor transmitted through an ignited glass tube, is resolved into a species of oxy-carburetted hydrogen gas, of greater

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* Nicholson's Journal, 4to, vol. ii. p. 199.

specific gravity than the other gases of this family; which consumes a large quantity of oxygen in its combustion, and affords a large proportion of carbonic acid: it contains, therefore, a large quantity of carbon.

CAMPHORIC ACID produced by the decomposition of camphor, either by heat or by the action of nitrous acid, by the preceding processes, has some resemblance to Benzoic acid; but Lagrange, in a memoir on this subject [*], and afterwards Bucholz [†], have pointed out essential differences of properties. It has an acid bitter taste, and reddens infusion of litmus. Its crystals are plumose and white; they effloresce on exposure to the air: they require 100 parts of cold water for their solution, but not more than 10 parts of boiling water. Alkohol dissolves its own weight of this acid, and with the aid of heat one half more. When the acid is placed on ignited fuel, it emits a dense aromatic vapour, and is dissipated. By applying heat to it in close vessels, it melts and sublimes; by a higher heat its properties are changed; it no longer reddens litmus, it acquires an aromatic smell, its taste is less penetrating, and it is no longer soluble in water.

The salts formed by this acid are named CAMPHORATES. Their taste is bitter: they are decomposed by heat, the acid being sublimed; and they exhibit a blue flame when heated before the blowpipe. Camphorate of potash is white and transparent; is sparingly soluble in cold, but abundantly soluble in boiling water, and crystallizes from its hot solution. It is also soluble in alkohol. It is slightly deliquescent in a humid atmosphere; is fused, and decomposed by heat, and burns with a blue flame. Camphorate of soda is less soluble either in cold or warm water: its crystals are not regular; they are white and transparent, and have a bitterish taste; are slightly efflorescent; soluble in alkohol. Camphorate of ammonia is not easily crystallized: its solution, evaporated by a gentle heat, giving a solid matter, not transparent, which has nearly the same solubility as the camphorate of potash. It is deliquescent, and soluble in alkohol. Camphorate of lime remains in solution when formed by adding the acid to lime-water. According to Bucholz, it dissolves in five parts of cold water. By evaporation it crystallizes in plates, of a white colour; which are efflorescent: it is insoluble in alkohol. The camphorate of barytes is obtained by evaporation, in crystalline plates. It is very sparingly soluble in water; is not altered from exposure to the air. Its taste is slightly bitter. Camphorate of magnesia, prepared by adding camphoric acid to carbonate of magnesia diffused in water, is deposited, after evaporation, in crystalline plates, white, opaque, and slightly efflorescent. Its taste is bitter; it is very sparingly soluble in water and in alkohol. Camphorate of argil, prepared by a similar process, is deposited, on evaporation and cooling, in a white powder, having a taste somewhat bitter and styptic. It is soluble in about 200 parts of cold water, and in a less quantity of boiling water. It is also sparingly soluble in alkohol. It is decomposed by heat, and, like the other camphorates, burns with a blue flame.

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[*] Annales de Chimie, tom. xxvii.

[†] Nicholson's Journal, vol. xxxii. p. 151.

CAMPHOR has been supposed to be capable of being artificially formed. Kind, a German chemist, in forming a medicinal preparation, by passing muriatic acid gas through oil of turpentine, observed that "the oil acquired a brown colour; and after cooling, the liquor was almost wholly coagulated into a crystalline mass, which in every respect comported itself like camphor." He farther remarked, that though a similar production of camphor had not been before noticed, yet Meyer speaks of a concretion of a camphoric nature, formed in oil of turpentine, digested with dry caustic salt; and Trommsdorff observed a formation of camphor, on distilling essential oils on lime.

Trommsdorff repeated Kind's experiment, and obtained similar results. A concrete matter was procured, which, when dry, was white and semi-transparent: its odour was strong, and analogous to that of camphor. When heated, it is volatilized, without any residuum: in close vessels it sublimed; in the open air its vapour inflamed. It was dissolved by alkohol, and was precipitated unaltered by water. It dissolved with facility in almond oil. Concentrated nitric acid effected its solution, at first calmly, but afterwards with a disengagement of nitric oxide gas. The mixture became turbid by the addition of water, but did not deposite camphor,—the only circumstance attending these experiments in which this substance differed from common camphor, and which Trommsdorff supposed might be owing to the presence of a little muriatic acid, or oil of turpentine.

These experiments were repeated by Boullay, in conjunction with Cluzel and Chomet, who added several facts connected with this artificial formation of camphor [*].

From four pounds of oil of turpentine, put into the first bottle of Woolfe's apparatus, and submitted to the action of the quantity of muriatic acid gas disengaged from four pounds of sea-salt and two pounds of sulphuric acid, they obtained twenty ounces of a crystalline matter: on the liquid having stood several days, four ounces more were deposited; and on exposing it to intense cold, two ounces more were obtained, thus affording, on the whole, seven ounces and a half of this matter for each pound of oil of turpentine employed.

This matter, washed in distilled water, became of a beautiful white colour: it gave no signs of acidity, but had an odour of turpentine. When washed with water having dissolved in it carbonate of potash, it lost much of this odour. When mixed with an equal quantity of charcoal powder, of quicklime, or of dry argil, and sublimed, a mass of needle-formed crystals was obtained. Thus purified, it lost the smell of oil of turpentine, and had one analogous to that of camphor, but not so strong. It swims on water, and communicates to it its taste: it is dissolved in alkohol, from which it is separated by water unaltered.

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[*] Nicholson's Journal, vol. x. p. 152.

So far in its properties it is the same with natural camphor: in others, however, it is different. Nitric acid diluted, which dissolves common camphor, had no effect on it. The concentrated acid had at first no action on it; but, after a few seconds, a solution is effected, nitric oxide gas being disengaged; while the same acid dissolved common camphor, diffusing white vapours. Neither did acetic acid, which dissolves common camphor, act upon this artificial substance in the cold. On applying heat, it softened, and seemed to dissolve it; but, on cooling, it was collected unaltered on the surface of the acid.

The French chemists found, that when oil of turpentine was kept for three days in a sand-bath, the temperature of which was about 120°, a light and volatile oil was condensed in the receiver, and in the capital many small crystallizations of camphor; but they conclude, that although this appears to prove that camphor exists in this oil, it could not have contained so large a quantity as that obtained by the action of muriatic acid gas on the oil; part at least, therefore, of which must have been formed during the process. The other volatile oils afforded no camphor when subjected to the action of muriatic acid gas.

Thenard more lately submitted these products to examination. Kind had supposed, that the acid caused the formation of the camphor, by determining the combination of the hydrogen and oxygen of the oil, so as to leave carbon predominant. Gehlen advanced a different theory. Observing that only a part of the oil is converted into this product, the remainder forming a brown liquor of great acidity, and that not only this liquor, but also the crystallized matter, contains muriatic acid, he concluded, that the greater part of the hydrogen of the oil combines with a small quantity of carbon, and with a certain proportion of the muriatic acid, to form the concrete camphor; the remaining principles of the oil combining with the rest of the acid, and forming the dark-coloured liquid. Thenard repeated his experiments. The concrete matter, he found, lost, on exposure to the air, the property of reddening litmus, and it yielded only very minute quantities of acid when washed with alkaline solution; yet when it was sublimed, acid was separated from it; and a still larger quantity was evolved when it passed through an ignited tube. He supposed, therefore, that the camphoric concretion is merely a compound of the essential oil and of a portion of the acid. He had obtained a similar product from the action of muriatic acid on other essential oils, as those of lemon and lavender; and he supposes that the camphor occasionally deposited from some of these oils, and even the camphor of the *laurus camphora*, may be a compound of essential oil with a vegetable acid *.

No very satisfactory proof is given by Thenard of his theory of the nature of these combinations; and there is more probability *a priori* in the supposition, that the oil should suffer some degree of decomposition by the action of the acid, than that it should merely combine with it. It appears to be established, however, by the experiments both of Gehlen and Thenard, that this product contains a portion of acid, either combined with the entire oil, or with its principles in certain proportions; and if natural camphor do not contain any acid, there remains the singularity of a product so analogous to it, being formed by a combination of muriatic acid with vegetable matter.

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* Memoires d' Arcueil, tom. ii. p. 27. or Philosophical Magazine, vol. xxxiv. p. 440.

SECT. XII.—OF RESIN.

THE principle to which this name is given, is one of those, the characters of which are most distinct and obvious. It is often in combination with some of the other principles, particularly with gum, essential oil, and extract. But there are vegetables which exude juices that concrete into a matter entirely resinous, and it is from these that the characters of the species are taken. The essential characters—are existing in the solid form, being insoluble in water, but soluble in alkohol, and in essential and expressed oils, and being incapable of being volatilized without decomposition.

The resinous juices obtained by spontaneous exudation, or from incisions in the vegetables affording them, contain a portion of essential oil, which, from exposure to the air, is either volatilized, or changed so as to be converted into resinous matter, or sometimes the oil is abstracted by distillation. When combined with gum or extract, it can only be separated by a chemical process; and the usual one is, to dissolve the resinous matter by alkohol, and precipitate it by the affusion of water.

Resins, when concrete, are brittle, and have a smooth and conchoidal fracture; their lustre is peculiar; they are more or less transparent, and of a colour usually yellow or brown: they are often odorous and sapid, though some resins are insipid and inodorous.

Resins are fusible, and melt from a moderate heat. They are not volatile: for although, when strongly heated, a vapour arises from them, this is either from a portion of volatile oil which has adhered to the resinous matter, or is the result of decomposition. They are inflammable, and afford in their combustion, water, carbonic acid, and a dense smoke which condenses into a fine charcoal. When subjected to decomposition by heat in close vessels, they afford water, a portion of acid, carburetted hydregen and carbonic acid gases, and a residuum of charcoal. They are, therefore, compounds of carbon, hydrogen, and oxygen. The volatile oils appear to be convertible into resins by long exposure to the atmosphere; but it is not evident whether this is owing to the oxygen combining with the entire principles of the oil, or with its hydrogen, forming water, and leaving the oil with an enlarged proportion of carbon and oxygen.

From the analysis of resins by Gay Lussac and Thenard, it appears that they resemble the oils in containing more hydrogen in proportion to the oxygen, than that proportion of these elements which constitutes water. The proportions of the resin of turpentine, they state at 75.944 of carbon, 13.337 of oxygen, and 10.719 of hydrogen. The proportions of the resin of copal are 76.811 of carbon, 10.606 of oxygen, 12.583 of hydrogen.

All the resins are insoluble in water, and are not affected by this fluid. Neither do they suffer alteration from exposure to the air; hence from both qualities, they are used as the basis of varnishes, with which the surfaces of substances are covered, that require to be protected from the action of air and humidity. In a very humid atmosphere, however, they become soft.

Resins are soluble in alkohol; some of them more sparingly than others. Those which are most difficultly soluble, have their solubility promoted by the addition of camphor. Their solutions are decomposed by water, and the resinous matter is precipitated. They are soluble likewise in ether, and in volatile and expressed oils: camphor exerts a marked action on them; when beat with any resin or gum-resin, it renders it soft and nearly liquid.

Resins combine with the alkalis. Mr Hatchet, in examining the substance known by the name of Lac*, which consists principally of resin, found, that it was completely soluble in solutions of potash and soda, forming saponaceous compounds, which are decomposed by acids, and the resins again precipitated. And he found, that other resins gave similar results. Facts of this kind had been known to the older chemists: thus copal, which of all the resins seems to be least easily acted on, was known to be dissolved by pure alkalis, the solution being precipitated by acids †: and common resin enters in considerable quantity into the composition of the coarser soaps. The alkaline carbonates, and even salts, having a slight excess of alkali, as common borax, exert a similar action, only less energetic. The solvent action of ammonia on the resins, is not so complete as that of the fixed alkalis.

Resins are soluble in some of the acids, and by others are decomposed. On this subject the most accurate information is to be derived from Mr Hatchet's experiments ‡. Sulphuric acid poured on any resin in powder, dissolved it, he found, in a few minutes: the solution being transparent, of a yellowish brown colour, and an oily appearance: progressive alterations take place in the dissolved matter: the principal product of which in a certain stage of the process, is a substance which has the properties of the vegetable principle named Tannin; this, too, is changed by the continued action of the acid, and is ultimately converted into charcoal. Nitric acid acts on resins; it does not dissolve them; but, as Mr Hatchet remarks, decomposition to a certain degree precedes solution: it first converts the resinous matter into a pale orange-coloured, brittle, porous substance, then into a product which has the intermediate characters of vegetable extractive matter and of resin; and, lastly, into a variety of the tanning substance.

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* Philosophical Transactions, 1804.

† Materia Medica Bergii, p. 899.

‡ Philosophical Transactions, 1804, 1805, 1806.

There is one acid which appears to be a direct solvent of resins, without materially altering their composition,—the acetic acid. Mr Hatchet observed its solvent power, in his analysis of lac; the whole of the resin of that substance being dissolved by it, with the assistance of heat, a portion being deposited as the liquid cooled, and a part remaining dissolved, which was precipitated by water.

A number of resinous substances are met with in commerce, being used in medicine or the arts; such as copal, sandarach, mastic, dragon's blood, elemi, and the resins obtained from the juices of the different species of pine. These, though a general analogy exists among them, differ somewhat in their chemical properties, so as to lead them to be regarded as varieties of one chemical species. They hence require some separate notice.

The juices of different species of Pine consist principally of essential oil and resin; and in different states of preparation give rise to the varieties of Turpentine, Resin, Tar, and Pitch *. The native juices, obtained from incisions in the trunk or branches, have received the common name of Turpentine. Common turpentine is procured from the Pinus sylvestris: Venice turpentine, which is thinner, and contains more essential oil, is from the Pinus larix: Strasburg turpentine is the produce of the Pinus picæa: Canadian Balsam is a finer turpentine obtained from the Pinus balsamea. When these turpentines are submitted to distillation with the addition of water, the essential oil distils over, forming the oil of turpentine of commerce. The resinous matter remains, and is the com-

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* Journal de Physique, tom. xxxi. p. 337.

mon or yellow Resin of the shops. When the juice is melted from the wood of the tree, by the application of heat, it undergoes some decomposition; the wood also is charred; hence the product is a dark-coloured resinous liquid, consisting principally of empyreumatic oil, resin, and acetic acid. This constitutes Tar. This, when inspissated by boiling, forms Pitch.

Sandarach is the produce of the Juniperus communis. It is in small round fragments, of a yellowish colour, semitransparent, and brittle, having a slight odour, and scarcely any taste. It is soluble in alkohol, and is used in the composition of some of the spirit varnishes: it is not soluble in oil or melted tallow, in which it differs from resins.

Mastich is the produce of the Pistacia lentiscus: it is in small rounded masses, of a yellowish colour, semi-transparent; has scarcely any taste, and its smell is perceptible only when it is heated. It is soluble in alkohol, but not entirely. Mr Matthews found, that nearly a fifth part remains undissolved: this residual matter, after repeated washings with alkohol, is white, elastic, adhesive, and inflammable, and seems to approach to caoutchouc in chemical properties *. It differs from it, as Mr Brande has remarked, in becoming hard when dried, by exposure to the air.

Copal is a resin possessed of peculiar properties, and valuable, as forming the finest varnishes. It is the produce of the Rhus copallinum, a native of Mexico: it is in rounded masses, smooth and brittle, transparent, or nearly so, without colour, or having only a slight tinge of yellow: its taste is weak, and it has scarcely any smell: when chewed, it does not become tough, as mastich does: it is fusible, inflammable, and insoluble in water. The property in which it differs from the greater number of resins, is its very sparing solubility in alkohol: when digest-

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* Nicholson's Journal, vol. x. p. 247.

ed in that fluid, with the assistance of heat, part of it assumes the appearance of an opaque, soft, viscous mass; a small portion only is dissolved, and the greater part of this subsides as the liquid cools. It affords the best varnish, and hence a number of experiments have been made to discover a proper solvent of it. Camphorated alkohol dissolves the greater part of it; and a perfect solution is obtained, when camphor and copal are put together into alkohol, owing to the peculiar action which camphor exerts on all the resins. It is not soluble by digestion in expressed oils; but if it be melted, and the oil be dropt on it, it is dissolved both by fixed and volatile oils. By oil of turpentine, it is converted into a soft viscid-like substance; and if the oil be old, it acts more powerfully on the copal than when recent. Other oils, as those of rosemary and lavender, dissolve it in the cold. And as these three oils, especially when long kept, appear generally to contain camphor, it is probable that it promotes the solution of the copal.

Elemi is a resin little used. It is the produce of the Amyris elemifera; is in large solid masses, of a variegated greenish colour, and semi-transparent. It is fusible, inflammable, soluble in alkohol, and partially soluble in expressed and essential oils.

Animi, the produce of the Hymenæa courbaril, is a resin which, in its external appearance, has a strong resemblance to copal, and is often sold for it, or mixed with the real copal: it is distinguished by having more of a yellow tinge, by becoming somewhat ductile when masticated, and being more easily soluble in alkohol, and in essential or expressed oils.

The resin, named Dragon's Blood, is obtained from the Pterocarpus draco, and from some other plants. It is of a red colour, and variegated texture, opaque, hard, and friable; without taste or smell. It is fusible, inflammable, and soluble in alkohol, giving to it a deep red colour.

The substance known by the name of Lac is produced by an insect, which deposites it on the branches of certain trees in India, formed into cells, which appear designed as an envelope for its young. It is imported into Europe in different states,—stick lac, which is the substance in its natural state; seed lac, in which it is reduced into small grains by pounding, and from which part of the colouring matter appears to have been extracted by boiling; and shell lac, which is prepared from the natural lac, by liquefying, straining, and forming it into thin plates, and which contains least of the colouring matter. The lac, freed from the insect involved in it, has all the characters of vegetable matter, and is probably not formed, but deposited by the animal which produces it. Mr Hatchet found it to consist of resin, with colouring extract, vegetable gluten, and wax; the different varieties giving the following proportions *:

	Resin.	Extract.	Wax.	Gluten.
Stick lac,	68	10	6	5.5
Seed lac,	88.5	2.5	4.5	2
Shell lac,	90.9	0.5	4	2.8

The principal qualities of the lac are derived from the resin. Alkohol dissolves this, forming in the cold a transparent solution; but if it be heated, the solution is turbid. Ether acts less powerfully on it. Water acquires a crimson colour, more or less deep, according to the proportion of colouring matter. The stronger acids, as the sulphuric and nitric, decompose it. Muriatic acid dissolves its colouring matter, and gluten; acetic acid dissolves the whole of it, except the wax. The alkalis and alkaline carbonates dissolve it, forming saponaceous solutions; and it is also rendered soluble by borax. Lac is used in dyeing, and the preparation of paints; a solution of it in water, by the medium of borax, is the basis of the Hindoo ink, and may

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* Philosophical Transactions, 1804.

be used as a varnish. It enters into the composition of the common spirit varnishes, and is employed in the formation of sealing wax.

Besides the substances now described, which are nearly pure resins, resinous matter exists in combination with other proximate principles of vegetables, and is also contained in the leaves, bark, and other parts of plants. The medicinal powers of a number of important articles of the Materia Medica depend on a resinous principle in these states.

The principal use of the resins is in the formation of varnishes: which consist of resin in a state of solution. They are named Oil or Spirit Varnishes, as oil or spirit is the solvent. The oil may be either expressed or volatile. Of the former, the drying linseed oil is generally employed; of the latter, oil of turpentine. A varnish with the first is prepared by boiling the finer kind of common resin with a portion of mastich in linseed oil; and to this a portion of oil of turpentine is usually added, which accelerates the drying of the varnish. Copal is also used in the composition of these fat varnishes. These solutions of copal or mastich have been recommended for mixing with colours to be used in painting, the tints of colour being less injured, retaining their brilliancy longer, and not being so liable to be acted on by any solvent, as when the colours are mixed merely with the drying oils *. Varnish with oil of turpentine alone is prepared by dissolving in this oil the requisite proportion of mastich. If a finer varnish of this kind is required, it is formed from copal; but it has always been found difficult to dissolve the copal completely in the oil. Different methods have been proposed; that by the medium of camphor appears to be the best. This varnish is colourless and durable, and answers well for varnishing pictures. Spirit varnishes have the advantage over oil varnishes, of drying more speedily, but they are liable

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* Nicholson's Journal, 8vo, vol. i, p. 259.

to split, and scale off. The alkohol requires to be highly rectified: the resins employed are mastich, sandarach, lac, and copal; and frequently mixed together. A colourless varnish is obtained, by dissolving mastich or sandarach in alkohol; a portion of turpentine being added, to render the varnish less brittle. The solution of copal, however, is preferable, as being colourless; but there is with regard to it the same difficulty of dissolving it in alkohol as in essential oils; and to promote its solution, camphor is in this case also the best medium *. Another mode of preparing copal varnish is to dissolve it in oil of rosemary, and add alkohol to the solution gradually, a few drops only being added at a time. The incorporation of the viscid solution of the oil with the alkohol is thus effected, and by farther dilution a colourless varnish is obtained †. Lac forms a varnish which is coloured, and is hence used only in those cases where the colour is of no importance, or is of advantage, as in lackering brass, or in laying on a coloured ground. Amber is sometimes used with a similar view.

From the combination of lac with Venice turpentine, sealing wax is formed. Four parts of lac are melted with two of turpentine, and two of resin; and the composition is coloured red by the addition of one part of cinnabar and one of red lead, or black, by the addition of lamp-black.

THE name of GUM-RESIN has been given to a number of vegetable products, supposed to consist of gum and resin. Their nature, however, is not very well determined; they usually contain a matter that seems to be resinous; the existence of gum in them is more doubtful. A num-

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* Nicholson's Journal, 4to, vol. iii. p. 447.

† Ibid. 8vo, vol. ix. and vol. xxiv. p. 67.; and Aikin's Chemical Dictionary, article Varnish.

ber of medicinal substances,—such as aloes, ammoniac, assafœtida, euphorbium, galbanum, gamboge, myrrh, sagapenum, and scammony, are of this kind. They are solid, generally brittle and opaque; have a strong smell, and a pungent or bitter taste. They appear to contain various proportions of resin. They also often contain extractive matter. Braconnot has given the analysis of a number of them *; and besides these principles, has found in some of them portions of wax and of vegetable gluten. Aloes, which has usually been ranked as a gum-resin, he found neither to afford gum nor resin, and he therefore considers it as a peculiar principle. Trommsdorff however had found resin in it with what he named saponaceous extractive matter; and Lagrange and Vogel concluded from their experiments, that it consists chiefly of resin and extract.

Gum-resins differ in their chemical properties, probably from the diversity in the proportions of their immediate principles. In general they are only partially soluble in alkohol or in water; the former dissolving the resin, the latter principally the gummy or mucilaginous part: but in each case, part of the one principle appears also to be dissolved by the medium of the other; probably in consequence of their mutual affinity; and those in which resin predominates are even entirely soluble in alkohol, while these in which gum or extract is abundant are soluble in water. They are almost all entirely soluble in diluted alkohol, consisting of equal parts of alkohol and water; and many of the tinctures of the shops are solutions of this kind. By trituration with water they form milky mixtures; the resin being suspended by the medium of the other matter. They are soluble in alkaline liquors, forming solutions somewhat saponaceous. The more powerful acids decompose them, but from Mr Hatchet's experiments they appear to be less susceptible than the resins of afford-

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* Nicholson's Journal, vol. xxvii. & xxviii.

ing, by these decompositions, artificial tannin. Nitric acid, by its action on some of the gum-resins, forms a portion of what has been named the bitter principle.

The gum-resins when heated soften, and, if the heat is raised sufficiently high, are decomposed. In destructive distillation they afford ammonia, with the usual products of vegetable matter.

The consideration of the different gum-resins belongs rather to materia medica or pharmacy, than to chemistry. The medicinal powers of many vegetables appear to depend on such combinations.

GUAIAC, a substance obtained by spontaneous exudation from the Guaiacum officinale, has been considered as a gum-resin, containing a large proportion of resin. From Brande's experiments*, it appears to possess some chemical properties, indicating a peculiarity of composition.

Guaiac is concrete, brittle, and resinous in its appearance; it is of a grey colour, but assumes a greenish colour, from the action of the air: it assumes the same colour in oxygen gas: and this property is one character which discriminates it from the resins. When digested in water with a moderate heat, a small portion is dissolved, which appears to be extractive matter, with a little lime. Alkohol dissolves it, leaving a little foreign matter, not exceeding 5 parts in 100, undissolved. The solution is rendered milky by water; and is decomposed by different acids, with phenomena that are peculiar. Muriatic acid throws down an ash-coloured precipitate: liquid oxymuriatic acid, one of a beautiful pale blue. Sulphuric acid, when not in too large a quantity, separates the resin of a pale green colour. Nitric acid, diluted with one-fourth of its weight of water, causes no precipitate until after some hours: the liquid assumes a green colour, and if water be added, a green precipitate may be obtained: the green colour soon changes to blue, when, by the same means, a blue precipitate may be obtained: it then becomes brown, and a brown precipitate falls down. These changes of colonr are peculiar to guaiac, and appear to be connected with changes of oxygenation.

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* Philosophical Transactions, 1806.

Muriatic acid dissolves a small portion of guaiac, the solution assuming a deep brown colour. Sulphuric acid forms with it a deep red liquid, which, when fresh prepared, deposites a lilac coloured precipitate on the addition of water: if heat be applied, the resin is decomposed and charred. Nitric acid exerts a strong action on guaiac; even in the cold the powder assumes a dark green colour: there is a violent effervescence from the emission of nitric oxide gas, and the whole is dissolved. The solution, after it has stood for some hours undisturbed, deposites oxalic acid. Diluted nitric acid causes a slight effervescence, part of the resin is dissolved, and the remainder is converted into a brown substance, which Mr Brande supposes, is the last result of the oxygenation of guaiac. It has more completely the properties of resin, is soluble in alkohol, and in ether, which guaiac is very sparingly; it is also insoluble in water. If fresh portions of nitric acid be added to it successively, it becomes equally soluble in water and alkohol, and acquires an astringent bitter taste, forming probably one of the varieties of artificial tannin.

Guaiac is soluble in the alkalis, and in the alkaline carbonates, forming greenish brown liquids. Hence they do not precipitate it from its solution in alkohol.

From these properties of guaiac it appears, that although it is similar in many respects to resins, it differs in others: particularly in affording extractive matter; in the changes of colour it suffers from the action of oxygen and of acids; in being capable of being converted into a more perfect resin ; in yielding oxalic acid, when treated by nitric acid ; and in the large quantity of charcoal and lime which it yields on destructive distillation,—differences which probably arise from certain peculiarities in the proportions and chemical combination of its elementary principles.

The substances named **Balsams**, consist of resin, with a quantity of the vegetable acid named Benzoic, and generally a portion of essential oil. The same remark applies to them as to the gum-resins,—that they cannot properly be regarded as constituting a distinct proximate principle of vegetables, since they are rather a mixture or combination of other known principles. Some chemists indeed, as Gren, have supposed, that the benzoic acid which they afford does not previously exist in them, but is formed in the process by which it is extracted. But the various processes by which it is procured, are unfavourable to this conclusion. It is separated from the balsams by the application of heat, by boiling or macerating them with water, or with alkaline solutions, or digesting them with acids ; and it is not very probable, that agents so different in their chemical actions should give rise to the formation of the same product. The action of some of them, too, appears not sufficiently energetic, to be capable of producing such an effect. The heat that requires to be applied to volatilize the acid from the balsams, is very moderate ; and we have no example in which water, by any affinity which it exerts, *causes* the formation of a new principle. It appears therefore more probable, that this acid pre-exists in the balsams, and that it is only extracted by the processes by which it is obtained.

Their chemical properties are derived from the principles of which they consist : when exposed to heat, they melt like the resins, and exhale a fragrant and acrid vapour, which is the benzoic acid, and which condenses in needle-like crystals. If heated more strongly, a portion of oil is volatilized: subjected to destructive distillation, they afford, besides benzoic acid, products similar to those from the resins: heated in the open air, they inflame.

They are insoluble in water; but by digestion with it benzoic acid is dissolved, which may be obtained, by evaporation and cooling, crystallized. According to Fourcroy, their powder, when mixed with the vegetable colours diffused in water, reddens them,—a proof of the presence of free acid. When distilled with water, a small quantity of essential oil is obtained from the greater number of them.

They are soluble in alkohol; and the solution is decomposed by the affusion of water, the resinous matter being precipitated. It is also decomposed by some of the acids. They are soluble in ether, and in the volatile oils, and are softened by the action of camphor.

The action of the alkalis on the balsams, is similar to their action on the resins,—dissolving them and forming brown solutions. The alkali combines also with the benzoic acid; and on saturating it with an acid, benzoic acid is precipitated. The action of lime, by the medium of water, is similar.

The stronger acids, particularly the sulphuric and nitric, when digested on the balsams, caused, in Hatchet's experiments, a formation of tannin. There was also, in some cases, a formation of prussic acid; and benzoic acid was obtained by sublimation from the mixture. This acid is not decomposed by sulphuric or nitric acids; hence its appearance in this process, supposing it to pre-exist in the balsams. Acetic acid, when heated, dissolves some of the balsams, as benzoin: it retains the resin in solution, but as it cools, allows the benzoic acid to precipitate.

All the balsams are odorous, and pungent. Some of them, as benzoin, are solid; others are fluid, but thick; these by age likewise become solid: they exude from the vegetables which produce them, either spontaneously or from incisions made in the bark. The principal substances of this class, are Opobalsam, or Balsam of Gilead, the produce of the Amyris gileadensis; Balsam of Peru, from the Myroxolon peruiferum; Balsam of Tolu, from the Toluifera balsamum: Benzoin, from the Styrax benzoinum; and Storax, from the Styrax officinale. They are used sometimes in the practice of medicine, and their individual history belongs to the materia medica.

SECT. XIII.—OF EXTRACT, OR EXTRACTIVE MATTER.

THE name of Extract has, in pharmacy, been appropriated to a preparation in which vegetable juices, or the watery decoctions of vegetable substances, are reduced by evaporation to a thick consistence. From the nature of this process, it is evident, that the product may consist of all those principles which are soluble in water, and that, as obtained from different plants, it may be very different. Preparations of this kind being much used in the medical practice of France, have always engaged the attention of the French chemists. Rouelle arranged them under three classes; Mucilaginous extracts, soluble in water, in which gum or mucilage predominates; Resinous extracts, containing chiefly resin, and which are hence more especially soluble in alkohol; and Saponaceous extracts, which are soluble both in water and alkohol. A different view has since been taken of this subject: it has been supposed, that though in these preparations there may be an intermixture of principles, there is one which forms their basis, and which constitutes a peculiar vegetable principle, distinct from any other. It is to denote this, that the name Extract, or Extractive Matter, is applied. This view has been principally given by Fourcroy and Vauquelin, in their analysis of different vegetables: by the former particularly, in his analysis of the cinchona of St Domingo *, and by the latter, in his analysis of the sap of vegetables †. Hermbstaedt also stated some facts with regard to it. The extractive principle thus defined is synonymous nearly with the saponaceous extract of Rouelle. Schrader has accordingly affirmed that they are the same ‡, while Grotthus has more lately contended that they are different ||. And there is, as I shall have to remark in concluding its history, a considerable degree of doubt as to the nature of extract; whether it can properly be regarded as a well-defined proximate principle or not. The term Extract is ambiguous, from the signification under which, in the language of pharmacy, it is still understood. Were its existence established, the name Extractin would be free from this ambiguity.

Extractive matter exists in different parts of plants, but more particularly in the leaves, bark, and wood: it is also often dissolved in their juices. When it exists in the solid parts, it is obtained by boiling in water, and evaporating the strained decoction: when in the juice, it is obtained by evaporating this by a gentle heat. In either case it is obvious that it may be mixed with other principles: there is no process by which these can be separated, so that we are certain of obtaining it pure: and hence its properties are discovered, either from examining it as afforded by some vegetables with little intermixture, or from effects re-agents produce upon the juices or decoctions containing it, which cannot be supposed to arise from the operation of these on other known principles.

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* Annales de Chimie, tom. viii. & ix.

† Ibid. tom. xxxi.

‡ Nicholson's Journal, vol. xxxii. p. 75.

|| Annals of Philosophy, vol. vii. p. 47.

Extractive matter is soluble in water, but it gradually becomes insoluble from exposure to the air. According to Vauquelin, the juices which contain it, are colourless as they issue from the plant, but assume a yellow or brown colour, from the action of the air and light. If evaporated, a pellicle forms on their surface, from the undissolved matter becoming insoluble; and when the whole is reduced by evaporation to a thick consistence, on attempting to dissolve this in water, a portion remains undissolved. Fourcroy has observed too, that if the decoction of a vegetable which affords extract, be filtered, so as to be transparent, by merely continuing to boil it, it becomes turbid: the longer the boiling is continued, and the more freely the liquor is exposed to the air, the more insoluble matter, he adds, is formed; and by continuing the successive solutions and evaporations, the whole may be brought into this state.

This change he ascribes to the absorption of oxygen: and assigns this as a property characteristic of this principle,—that it is soluble in water, but when in solution, and at a high temperature, absorbs oxygen and becomes insoluble, and comparatively insipid and inert. The injury which many medicinal plants sustain from boiling, has been ascribed by Fourcroy to this cause, and not to the dissipation of any active volatile principle, as had been supposed; and indeed from many of them which are injured by this operation, no such principle is obtained, when the operation is performed, so as to collect the products.

Theodore Saussure has remarked, that Fourcroy, in ascribing these changes to oxygenation, does not affirm that he had submitted the insoluble matter to analysis, or the air, in contact with which the liquid had been boiled, to any eudiometric trial. He therefore placed, under bottles full of atmospheric air, and closed by quicksilver, capsules containing solutions of the extractive matter of cinchona, oak-wood, and different moulds: after some days, he found precipitates had formed in these solutions, and the air had suffered a small diminution of volume. Submitted to eudiometric examination, it was found to have lost its oxygen, which was replaced by a quantity of carbonic acid gas, not exactly equal in volume to the oxygen that had been consumed, as part of it had been absorbed by the water of the solution; but when this was previously saturated with carbonic acid gas, the quantity was equal to the quantity of oxygen that disappeared. He further found reason to conclude, that in thus losing part of their carbon, they lose still more of their oxygen and hydrogen, by these principles entering into combinations and forming water, and that the residual insoluble matter has an enlarged proportion of carbon, and is not merely, as Fourcroy had inferred, extract oxygenized *.

Extractive matter is soluble in alkohol: and this solution is not decomposed by the affusion of water. This may therefore be regarded as another characteristic property of extract, and as serving to distinguish it from gum, resin, or any mixture or combination of these; gum being soluble in water, and not in alkohol,—resin in alkohol, not in water. Gum-resin is indeed partly soluble in either fluid, but it never is entirely so; since, if it contain so much gum as to be soluble in water, it is partially dissolved by alkohol; or, if it contain so much resin as to be soluble in alkohol, it is imperfectly dissolved by water. And if a gum-resin be digested either with water or alkohol alone, the solution it affords with the one fluid is decomposed by the other. Schrader has affirmed, however, that extract is soluble only in diluted alkohol, and not in pure alkohol †, a proof of the imperfect distinction of this principle.

According to some chemists, extractive matter is inso-

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* Recherches sur la Vegetation, p. 156.

† Nicholson's Journal, vol. xxxii. p. 76.

luble in ether. This, if the observation were just, would afford a very characteristic property of this principle. I have found, however, that sulphuric ether dissolves the colouring matter of saffron, which has usually been given as an example of pure extract, and which appears to be so *.

Oxymuriatic acid, poured into a solution of extractive matter, converts it into a concrete substance of a yellow colour, insoluble in water, but soluble in alkohol, and in the alkalis †. If cloth be steeped in oxymuriatic acid, and then immersed in a solution of extract, the oxygen is transferred from the acid to the extract, which is then deposited on the cloth, and adheres to the vegetable fibre. Vauquelin precipitated the extractive matter from the vegetable juices which he examined, by oxymuriatic acid.

This principle has an attraction to alumina, and to metallic oxides. If to a solution of it in water there be added a solution of alum, of which the excess of acid has been previously saturated, on boiling them for a short time, an abundant flocculent precipitate is formed, composed of the extract combined with the earth of the alum; and the solution at the same time is nearly deprived of its colour. If cotton or thread impregnated with a solution of alum, be macerated in a solution of extract, it becomes tinged of a yellowish brown colour, from the extractive matter being fixed in it by the medium of the alum; and in this way the solution may at length be deprived of nearly all its dissolved matter, and the cloth dyed. Many of the

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* Lagrange and Vogel have lately considered the soluble matter of saffron as a peculiar principle, different from extract, and have given it the name of Polychroite. There seem, however, to be no essential characters referred to it. The most important are, its losing its colour from exposure to the air, becoming of a dark blue colour from the action of sulphuric acid, and of a green colour from the action of nitric acid, (Annales de Chimie, tom. lxxx.).

† Fourcroy, Annales de Chimie, tom. vi. p. 180.

metallic salts have a similar effect. The solution of muriate of tin, in particular, forms in the solution of extract an abundant flaky precipitate, of a brown colour, consisting of this principle in combination with the oxide of tin. The muriate in which the metal is at a high degree of oxidation, Dr Bostock found to be that which forms the most delicate test of extract *. It is less valuable, however, as a test, as it precipitates other vegetable principles, particularly tannin.

Extractive matter, in a humid state, suffers decomposition. Its watery solution gradually becomes turbid, deposites mucous flakes, becomes mouldy at the surface, yields ammonia, and, when the putrefaction is complete, leaves carbonates of potash and lime.

When subjected to destructive distillation, it affords an acid in part saturated with ammonia.

Such are the characters assigned to this principle; the most distinctive of which are, its equal solubility in water and alkohol; its susceptibility of oxygenation, and forming, when it has undergone that change, an insoluble matter; and its affinity for alumina and metallic oxides. It is afforded by many vegetables, in different quantities, and perhaps also of variable purity. Saffron affords a large proportion of it, and that nearly pure; 16 ounces of it yielding, it is stated, 10 ounces of extract, the remaining parts being principally ligneous fibre. Valerian is said to afford it in as large a quantity as saffron. It exists in gentian, senna, ipecacuan, and a number of leaves and roots. Opium and Peruvian bark contain a principle which so far has the characters of extract, that it is precipitated and rendered inert when boiled in water, with the contact of the air. It is contained also very generally in the juices of plants, obtained either from incisions of the growing plant, or from expression of their succulent parts.

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* Nicholson's Journal, vol. xxiv. p. 211.

I must add, however, that the characters of this principle, as obtained from different vegetables, are not uniform, and that sometimes it approaches in its properties to other principles. Thus, the active matter of Peruvian bark has one of the characters of extract, that of absorbing oxygen when in a humid state, or when boiled in water: but it approaches to resin, in being more soluble in alkohol than in water. The case is the same with the extractive matter of opium, while, in other vegetables, the reverse obtains; thus, the extractive matter of gentian appears to be more soluble in water than in alkohol.

Nor are the characters which have been assigned to it so distinctive, but that they may be presented by other principles from mixture or combination; and it is in such states that it has usually been obtained. Thus, in the juices of plants submitted to examination by Vauquelin, as yielding extract, he always found portions of saline matter, particularly of free acetic acid, and of the acetites of potash and lime. These might so far modify the principles existing in the juice, as to disguise their properties; acetic acid, for example, would render a portion of resinous matter soluble in water; and hence the peculiar properties which the vegetable matter did present might arise from these modifications, and not from the presence of any peculiar principle to which they belonged. From this the solubility in water of principles otherwise not soluble might originate; and the properties of absorbing oxygen, or exerting affinities to certain earths or metallic oxides, are in some measure possessed by various vegetable principles; they may be exerted more readily by them in such a state of intermixture, and can scarcely, therefore, be regarded as distinctive of extract.

From these considerations, there is some reason to doubt of the existence, as a distinct proximate principle, of the matter to which the name of extract has been given.

The Extracts which are prepared in pharmacy, by inspissating expressed vegetable juices, or boiling vegetable matter in water, and evaporating the decoction to a thick consistence, are various in their composition. Those prepared by the latter process may contain mucilage, sugar, tannin, and a portion of resin. The inspissated juices, besides these, may also be in part composed of the vegetable acids, and of other saline bodies; and, from analysis, they appear always to contain acetates of potash, lime, and ammonia, often free acetic acid, and sometimes sulphate and muriate of potash and sulphate of lime. They usually redden infusion of litmus, exhale vapours of acetic acid when acted on by sulphuric acid, and give a smell of ammonia when mixed with lime. As obtained from different plants, they must vary in their composition. They appear also to be liable to decomposition on keeping; and the powers of the substances from which they are prepared are often injured by the decoction or inspissation: hence they are now little used in medical practice.

Sect. XIV.—OF TANNIN.

A number of vegetable substances, some of them inspissated exuded juices, others barks, or leaves, had received the name of Astringents, as possessed of the common property of astringency, characterized by the power of corrugating the animal fibre. From some chemical phenomena which they exhibit, it appeared, that they contain a common principle to which this quality is owing. If to their watery or spiritous infusion, a solution of any of the salts of iron be added, a purple colour is produced more or less deep. In those vegetables which have no astringency, no such effect is produced, while, in those possessed of this property, the deepness of the colour is in some measure proportioned to the degree in which it belongs to them. Hence it was concluded, that astringency in vegetables depends on a distinct principle. The Dijon Academicians observed, that it appeared to have some of the properties of an acid. Scheele discovered, that a peculiar acid exists in the excrescence which forms on the branches of the oak, known by the name of the Gall Nut, one of the most powerful of the vegetable astringents; and that it has the property of giving a purple colour to the salts of iron: it exists in all the powerful astringents; and being thus apparently connected with the property of astringency, it was regarded as the astringent principle.

To this conclusion Berthollet stated some very valid objections. He observed, that a solution of the gallic acid, when obtained pure, added to a solution of sulphate of iron, does not produce any dark colour or precipitate immediately, but only by degrees, and after some hours; while a small quantity of the infusion of galls instantly produces a more intense colour, and greater opacity. He farther found, that by two decoctions of galls in water, the acid is extracted from them, so that the liquors obtained by a third or fourth decoction do not redden litmus paper, nor afford gallic acid by evaporation, and yet they precipitate iron copiously from its solutions. There were even some kinds of galls, those of a white colour, as well as some other astringents, as sumach, or walnut-tree bark, which contain no sensible quantity of gallic acid, yet produce the black colour. And, lastly, the pure gallic acid has no sensible corrugating power, and scarcely even any astringent taste, but is merely sour *. These facts sufficiently

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* Elements of the Art of Dyeing, vol. i. p. 90. &c.

demonstrated, that the gallic acid is not the principle of astringency, but that this property must depend on some other principle, or on some modification of composition.

Deyeux, in his analysis of the gall nut *, inferred, that, besides the gallic acid, it contained a portion of extractive matter, and of what he considered as a kind of resin, or substance approaching to resin in some of its properties; that these are in a state of combination so as to be extracted, either by water or alkohol: and the astringent property he supposed to arise from this combination.

At length Seguin, in the course of some experiments on tanning †, established more clearly the existence of a principle in the vegetable astringents, different from the gallic acid, and in which the astringent or corrugating quality seems to reside. It is this principle which, from being the agent peculiarly concerned in the process of tanning, has received the name of Tan, or Tannin. It does not appear to be secreted pure by vegetables, or deposited in any of their parts in an insulated state, but requires to be extracted by certain processes, and, as obtained by these, is often mixed or combined with other principles, by which its properties are frequently modified. And from this circumstance, some doubts remain, as I shall have to remark in concluding its history, with regard to its specific distinction and characters.

It is contained in large proportion in the gall nut and in oak bark, sumach, and several other barks; and the catechu, kino, and other inspissated juices, consist principally of it in combination with extractive matter. If oak bark be macerated in water, the tannin and the gallic acid which are combined in it with the ligneous fibre are dissolved, forming a liquor of a dark-brown colour and a bitter acerb taste. If to the clear infusion a solution of the

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* Annales de Chimie, tom. xvii. p. 1.

† Ibid. tom. xx. p. 58.

animal principle named Gelatin, of which isinglass and glue are examples, be added, a flocculent precipitate or magma is formed, which subsides to the bottom; the liquor above contains the gallic acid, with any mucilage or extractive matter which may have been dissolved from the bark. A similar appearance results from the infusion of galls treated in the same manner.

This is the experiment of Seguin, by which he demonstrated the existence of a principle in the infusions of these astringents, the characteristic property of which is, forming with animal gelatin an insoluble compound, and in consequence of which property it can be withdrawn from other principles with which it is combined. It is obvious, however, that we do not thus obtain it pure, and that some additional steps are requisite to separate it from the gelatin with which it has been combined. Different processes have been employed for this purpose.

One proposed by Proust, consists in pouring a solution of muriate of tin into a decoction of galls: a precipitate forms from the combination of the tannin with oxide of tin: this is diffused in water, and a current of sulphuretted hydrogen is passed through: the sulphuretted oxide falls down, and the tanning principle remains in solution [*]. It is not pure, however [†]: the muriate of tin precipitates also the extractive matter contained in the vegetable infusion.

Another process proposed by Proust, is to pour a solution of carbonate of potash into infusion of galls. The tannin is separated in the state of a coagulum, which it is only necessary to wash with a little cold water to obtain pure [‡]. A similar process has been proposed by Bouillon Lagrange,—adding a solution of carbonate of ammonia to an infusion of galls, washing the precipitate with cold water, and then digesting it with alkohol until it cease to redden infusion of litmus; the residuum he considers as pure tannin *. But both these precipitates contain gallic acid and saline matter, chiefly a portion of the alkaline carbonate, and carbonate of lime.

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[*] Nicholson's Journal, 4to, vol. ii. p. 338.

[†] Ibid. 8vo, vol. ii. p. 198.

[‡] Ibid. 4to, vol. iv. p. 351.

A third process was proposed by Proust,—adding sulphuric or muriatic acid to a strong decoction of galls, a deposite is thrown down, which consists of the tannin in combination with the acid. It is washed with cold water; is dissolved in boiling water: the sulphuric acid is saturated by an alkaline carbonate, and the tannin is precipitated †. Still this is not pure, as extractive matter is also precipitated by these acids; and, from Davy's experiments, it appeared to contain likewise gallic acid.

Another method, proposed by Merat Guillot, consists in adding to a solution containing tannin, lime-water: a precipitate is obtained, which appears to consist of tannin combined with lime. If it be treated with diluted nitric or muriatic acid, the acid combines with the lime, and a matter so sparingly soluble as to remain on the filtre is obtained, which this chemist considered as pure tannin ‡. Davy supposed, that it must contain some of the extractive matter of the bark, and that it may likewise contain saline matter. It is, however, the simplest process, and perhaps affords purer tannin than the others; though a process is still wanting by which we can be certain of obtaining this principle in a state of purity; and indeed, from the force with which, according to the observations of Thenard, the vegetable principles combine with acids, it must be difficult to separate entirely tannin from the gallic acid with which it is usually associated. From his experiments it appears, that this acid exists in the gall nut in

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* Annales de Chimie, tom. lvi. p. 187.

† Nicholson's Journal, 4to, vol. iv. p. 352.

‡ Ibid. 8vo, vol. ii. p. 71.

very intimate combination with the tannin, that it is only as the tannin suffers spontaneous decomposition that the acid is entirely set free; and that there is no method by which the tannin can be obtained free from the acid *.

Tannin, in the forms in which it has been procured, by evaporation of its solution, is in the state of a loose powder, or a dry friable matter, having a resinous-like fracture. It is of a brown colour, or, according to Lagrange, of a white, which becomes brown from exposure to the air: has a peculiar smell, and a taste rough and bitter.

This principle is soluble in water, either cold or warm. It has been considered as being also soluble in alkohol; but, according to Richter, this is only when the alkohol contains water; when highly rectified, it is scarcely soluble in it †.

Tannin appears, from Seguin's experiments, to be susceptible of oxygenation. When its watery solution is exposed to the air, a pellicle forms on its surface, which becomes thicker the longer the fluid is exposed. It is still more quickly formed by exposure to oxygen, or to oxymuriatic acid; and from the latter thickens rapidly, so as to precipitate ‡. This may in part, however, arise from the extractive matter in the vegetable being acted on; and Seguin himself states, that infusion of tannin may be kept a long time without its properties being sensibly altered, even though it be not carefully secluded from the air. Lagrange, however, has affirmed, that tannin is very susceptible of oxygenation, and that by this change it acquires the property of reddening litmus, which otherwise does not belong to it.

Tannin is thrown down from its solutions by several of the acids. Sulphuric acid causes a dense whitish precipi-

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* Memoires d'Arcueil, tom. ii. p. 53.

† Philosophical Magazine, vol. xxiii. p. 75.

‡ Nicholson's Journal, 4to, vol. i. p. 275.

tate. The residual liquor separated by filtration was found by Davy still to precipitate gelatin, and therefore contained a portion of tannin. Muriatic acid produces similar effects, two compounds of the tannin being formed, one with an excess of acid which remains in solution, the other with an excess of tannin, which is precipitated. Nitric acid first renders the solution turbid; but the matter precipitated is soon re-dissolved with effervescence, and the liquor becomes clear, and of an orange colour. The tannin is decomposed during this action; for the liquid, after it, gives no precipitate with gelatin, even when the acid is saturated with an alkali. With dilute nitric acid a permanent precipitate is formed, and the residual liquid appears, from the test of gelatin, still to contain a portion of tannin. Lagrange has stated, that tannin is converted by oxymuriatic acid into gallic acid *. Were this established, it would point out the relation which appears to be so intimate between these two principles: and it might lead to the suspicion which some other facts suggest, that, in the processes to which they are subjected, the one is often converted into the other. It may be doubted, however, if this relation is so simple, as that gallic acid is tannin oxygenated; and the acidity acquired by the apparent oxygenation of tannin, may probably be owing rather to the decomposition of the tannin, and the developement of the gallic acid combined with it.

The alkalis combine with tannin. A solution of pure potash, poured into an infusion of galls, causes first a turbid appearance; but, by agitation, the fluid becomes clear, and its colour changes to brownish red. The solution of gelatin does not act on the liquid in this state of combination, until an acid be added in excess, and then a precipitation is occasioned. The action of soda is similar; as is that of ammonia. On heating the infusion to which

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* Annales de Chimie, tom. lvi. p. 191.

ammonia has been added, part of the alkali is volatilized, and the remaining portion acts on tannin, forming a quantity of insoluble matter, and leaving little in solution *.

Lime, barytes, and strontites, in solution in water, appear to combine with tannin, and form compounds of sparing solubility; since, when added to infusion of galls, a precipitation ensues, and the residual liquor gives no precipitate with gelatin. The precipitate of these earths with pure tannin is of a green colour. Magnesia boiled in the infusion forms a deep green fluid, which does not precipitate gelatin: the magnesia acquires a grey colour, and appears to have abstracted the tannin: the action of alumina appears to be similar †.

The alkaline carbonates cause a precipitation of tannin; the precipitate containing a portion of the alkaline carbonate, and, in consequence of this, it does not act on gelatin, until the alkali be saturated by an acid. The residual fluid of the infusion still contains tannin, which appears to be combined with a large quantity of the alkali, so as to remain soluble; and it also is incapable of acting on gelatin, until the alkali is saturated by an acid. The carbonates of lime, magnesia, and barytes, produce, in like manner, an insoluble combination of these respective earths with tannin: the residual liquid does not affect gelatin, even when an acid has been added to it; there is therefore no soluble combination of tannin formed in this case, as there is in that of the alkaline carbonates ‡.

Even a number of neutral salts, as nitrate of potash, muriate of soda, muriate of barytes, &c. cause a precipitation of tannin, apparently from their mutual attraction; and hence these precipitates contain a portion of the salt by which they had been thrown down.

The metallic oxides combine with tannin, forming compounds in general insoluble: some of them, as oxide of

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* Davy, Philosophical Transactions, 1803. † Ibid. ‡ Ibid.

tin, or oxide of zinc, boiled with infusion of galls, seem to precipitate it entirely, leaving only pure water. In consequence of these affinities, many of the metallic salts act upon this principle: they in general give rise to dark coloured precipitates, which consist of the tannin united with the metallic oxide, retaining frequently a portion of the acid with which it was combined. Acetate of lead forms a precipitate of a grey colour: nitrate of mercury, one that is yellow; sulphate of manganese is thrown down green: but these precipitates generally change their colour in drying [*].

The action of tannin on the salts of iron is important, from its relation to the art of dyeing, and to the composition of ink; and also as it forms the most delicate test of iron. The nature of this action is different according to the state of oxidation of the metal. If an infusion of galls, or of any vegetable astringent containing tannin, be added to a solution of the green sulphate or muriate of iron, it produces at first no change of colour, if the air is entirely excluded, and the solution has been free from air, otherwise the tint acquired is faint; but it deepens to a violet, which becomes nearly black on exposure to the atmosphere. If it be added to the solution of the red sulphate or muriate, the dark colour is at once produced. These facts appear to prove that the production of the colour depends on the state of oxidation, the deep colour being produced with the perfect oxide.

Berthollet has given a view of this subject somewhat different; he has shewn that the production of colour even with the green sulphate, may be produced by causes which do not change the oxidation. Thus, if the astringent infusion has been added to the solution of the green sulphate of iron without producing the violet colour, this appears on diluting it largely with water, or on adding a small portion of alkali, though the air is excluded; or even if a few iron filings be added to the mixed liquid in a flask, the violet colour is acquired, though their effect must be that of reducing the state of oxidation: on the other hand, it is prevented by a slight excess of acid. He supposes, therefore, that a high degree of oxidation of the metal is not essential to the production of the dark colour with tannin, but that this effect depends on the different force of affinity exerted by the acid of the salt to the oxide, its attraction being stronger to the oxide at a low degree of oxidation, and this counteracting the combination with the tannin, whence the colour would arise. Whatever weakens this affinity, therefore, favours the production of colour, though it may have no de-oxidating effect, such as dilution with water, the addition of a little of an alkali, or even of metallic iron; for the same reason the colour is at once produced with the red sulphate, the oxide in it not being retained in combination with the acid by so strong an attraction [*]. This view is probably just, though it also appears that iron in a high state of oxidation produces, independent of this, a compound with tannin of a darker colour, than it does in a lower state of oxidation. This is shewn by the fact that nitrous acid, added in a small quantity to a solution of the green sulphate with which tannin has been mixed, causes at once the production of a deep colour, which can only be ascribed to its communicating oxygen, for its direct operation, according to the above view, must be that of counteracting the combination.

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[*] Lagrange, Annales de Chimie, tom. lvi. p. 196.

The deep black colour, produced by the action of vegetable astringents on the red sulphate of iron, appears to arise from the action, not only of the tannin, but also of the gallic acid they contain; they combine with the oxide of iron; the precipitate is kept dissolved in some measure by the sulphuric acid: and it is this which forms the colouring matter of ink, and of the black dyes.

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[*] Chemical Statics, vol. ii. p. 252.

The most characteristic and important chemical property of tannin, is that of combining with animal gelatin. When its solution is added to a liquor containing gelatin, a precipitate, which quickly becomes flocculent, of a yellowish colour, is formed, and subsides: it is not putrescible; and on drying contracts and becomes hard and brittle, but resumes its softness, and a degree of tenacity, when it is moistened. The gelatin requires to be recently prepared: the quantity of precipitate is influenced by the state of concentration; the same quantities giving rather more precipitate, when strong solutions are mixed. It is influenced by the proportions; an excess of gelatin redissolving a little of the precipitate; and from Dr Bostock's observations there is reason to believe, that these principles combine in different proportions, so that in adding successive portions of solution of gelatin to infusion of tannin, the first portion unites with a large proportion of tannin, and forms a compound more insoluble than the succeeding ones. On an average, 100 grains of the compound of gelatin and tannin, formed by precipitation from saturated solutions, contain about 54 of gelatin, and 46 of tannin.

Gelatin, even in an indurated state, combines with tannin. A piece of animal skin, which consists principally of gelatin, immersed in an infusion containing tannin, discolours it, by attracting the tannin.

Tannin exposed to heat, affords an acid liquor, a brownish oil, and a considerable quantity of carbonic acid, leaving in the retort a light spongy coal *. Berzelius has endeavoured to determine the proportions of the constituent elements which these results indicate. To free the tannin from gallic acid, he added to an infusion of galls mixed with ammonia, muriate of barytes; the gallate of barytes

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* Seguin, Nicholson's Journal, 4to, vol. i. p. 274.

is soluble, while the tannate of barytes is insoluble. The tannin combined with the barytes he transferred to oxide of lead, establishing a combination which he found to be composed of 65.79 of tannin, and 34.21 of oxide of lead. He lastly decomposed the tannin of this by combustion, and from the quantities of water and carbonic acid formed, he inferred that it consists of carbon 51.160, oxygen 44.654, hydrogen 4.186 *. There must be some uncertainty, however, whether the tannin, in combining with the oxide of lead, does not suffer some change of composition, particularly from the formation of water.

This principle exists in many vegetables, and always in a state of intermixture with others, particularly with gallic acid, extract, and mucilage. Seguin has remarked, that the gallic acid is often unaccompanied by the tanning principle, as in cinchona, crude or roasted coffee, the roots of the strawberry plant, milfoil, scrofularia, arnica, and a number of others; these forming a dark precipitate with sulphate of iron, but not being affected by gelatin; but tannin, according to this chemist, is never found alone, but always accompanied with gallic acid.

Experiments were made by Davy on the principal astringents, with the view of determining the proportion of tannin they contain, and the principles with which it is united †; and some experiments on the same subject have been added by Bostock ‡, who has shewn by some just observations, the difficulty of discriminating these principles by the effects of re-agents, when they are in a state of mixture. In gall nuts, tannin is present in the largest proportion: 500 grains of Aleppo galls yielded to water, by lixiviation, in Davy's analysis, 185 grains of solid matter; of which 130 were tannin, 31 gallic acid, 12 mucilage and

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* Annals of Philosophy, vol. v. p. 184.

† Philosophical Transactions, 1803.

‡ Nicholson's Journal, vol. xxiv. p. 1. & 204.

extract, and 12 calcareous earth and saline matter. The proportions, however, are very various in different varieties: and the presence of some of these principles, particularly of the mucilage and extract, is even doubtful. The presence of the former has been inferred from the moulding to which infusion of galls is liable: that of the latter from the precipitate thrown down by muriate of tin. But Dr Bostock has remarked, that the production of mould cannot be regarded as a just indication of the existence of mucus, as it belongs to other principles. And with regard to extract, there is the uncertainty which belongs to the discrimination of this principle; independent of the circumstance, rendered probable by Dr Bostock's experiments, that tannin and gelatin combine in different proportions, forming compounds of different degrees of solubility, so that in the successive additions of gelatin to infusion of galls, a compound with tannin is at length established, which is not immediately precipitated; and to the presence of this remaining tannin, the farther slight precipitation by muriate of tin may be owing.

The bark and leaves of a number of vegetables yield a considerable proportion of tannin. Oak bark contains perhaps the largest quantity; one ounce, or 480 grains of the interior white bark, afforded 111 grains of solid matter by lixiviation, of which 77 were tannin. The bark of the Leicester willow afforded nearly the same quantity; that of the Spanish chesnut less; and the common willow and elm an inferior proportion. Sumach afforded as much as oak bark. Souchong and green tea gave also a considerable quantity. The quantities vary according to the age of the tree, and according to the season, as the experiments of Mr Biggin * have shown. The inner bark contains a larger proportion than the outer layers; and as the interior layers are comparatively more abundant in

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* Philosophical Transactions, 1799, p. 299.

young trees, their barks contain, in the same weight, a larger proportion of tannin than those of old trees.

The substance named Catechu, obtained by decoction and inspissation from the wood of the Mimosa catechu, is a strong astringent, and, from Davy's experiments, appears to contain a large proportion of tannin. It is almost wholly soluble in water: a considerable proporion of it is also soluble in alkohol, but, when acted on by the latter fluid, a portion of mucilage remains undissolved. One hundred grains of Bombay Catechu consists, according to these experiments, of 54.5 of tannin, 34 of extractive matter, 6.5 mucilage, and 5 residual matter, chiefly impurities. The same quantity of Bengal catechu gave 48.5 of tannin, 36.5 of extract, 8 of mucilage, and 7 of residual matter. The results however are doubtful, Dr Bostock having found the methods pointed out by Davy to separate these principles, to succeed very imperfectly. He found catechu always to contain a sensible portion of gallic acid.

Another astringent substance known in the shops by the name of Kino, and which is obviously either an inspissated juice or an extract, appears, according to the account of it given by Dr Duncan and by Vauquelin, to consist chiefly of tannin. Its solution gives a copious precipitate with gelatin, and throws down coloured precipitates from the metallic salts: that from the salts of iron is of a deep green colour. According to Vauquelin's experiments *, it consists of tannin, with a proportion of mucilaginous or extractive matter.

Proust remarked, that the tannin afforded by different vegetables is not uniform in its qualities; the tannin of catechu, in precipitating gelatin, does not form with it a magma of the consistence or insolubility of that formed by the tannin of galls; and it gives a violet-coloured ink with sulphate of iron. The tannin of kino forms

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* Nicholson's Journal, vol. vi. p. 234.

with the solution of glue a rose-coloured coagulum, and precipitates the salts of iron of a deep green colour, scarcely alterable by exposure to the air,—a property which also belongs to the tannin of rhubarb. The tannin of sumach, in precipitating glue, affords a white magma without consistence. Hence he concluded, that tannin has its varieties, like the other principles of vegetables; the property of precipitating gelatin being that which unites them, and as it were constitutes the species *. Some of these differences seem to arise from intermixture. Thus the infusion of sumach, Davy remarked, owes its property of being precipitated by the caustic alkalis to the presence of sulphate of lime; and to this may be owing the white colour of its precipitate with glue: that the infusion of galls is rendered green by the alkaline carbonates, depends on the large quantity of gallic acid it contains; and that the solutions of catechu do not copiously precipitate the carbonated alkalis, appears to depend on their containing tannin in a peculiar state of union with extractive matter, and uncombined with gallic acid or earthy salts †. In all cases, the power of combining with the acids, alkalis, and the earths, and the characteristic property of forming insoluble combinations with gelatin, and with skin, remain uniform, and seem to prove that the specific agencies of tannin are the same.

Some doubts, however, remain with regard to this principle. Its analogy to extract in many of its properties is obvious; and hence, as Schrader has remarked, they may be modifications of the same principle. The tannin of galls, as well as of many other substances, Thenard has found, cannot be obtained free from gallic acid; they seem to exist in very intimate combination, so that, in proportion as the tannin is decomposed, the gallic acid is more

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* Nicholson's Journal, vol. ii. p. 201.

† Davy, Philosophical Transactions, 1803.

abundantly developed; and we do not know the agencies of the matter with which the acid is combined, free from the acid itself*. Pure tannin, it is remarked by Pelletier, in some late observations on this subject, does not exist; the varieties of it which have been obtained differ in their properties,—their taste, solubility, &c. and have nothing in common but the property of forming with some of the varieties of animal matter, insoluble compounds, which are not liable to putrefaction, and of precipitating metallic solutions; and some of these properties belong to other vegetable principles. Extractive matter precipitates metallic oxides from their solution, and gallic acid forms with them combinations of dark colours; hence the joint action of these may produce changes similar to those from tannin. The property of combining with animal matter seems more specific, but this also belongs to some varieties of vegetable matter;—and, according to Pelletier, gummy and extractive matter, when joined to gallic acid, produces this effect, though neither of them do so when alone. In like manner gallic acid does not form a precipitate with the salts of iron, but gives merely a dark-blue colour, while infusion of galls forms a precipitate which is ascribed to tannin; but gallic acid acquires the same property of precipitating iron, according to this chemist, when it is combined with extractive matter †. These facts sufficiently prove, that the nature and relations of the principle denominated Tannin are still imperfectly known.

The artificial formation of a product analogous to tannin, is a subject which has been elucidated by a very extensive series of experiments by Mr Hatchet. It had been observed by Seguin, Proust, and Davy, that the tanning principle is developed in some vegetables by heat; and Chenevix found, that, in roasting coffee, tannin is evolved or produced so far, that after that operation its decoction gives a precipitate with gelatin *. Mr Hatchet observed some results in his experiments on the action of nitric acid on the resins, which led him to examine its action on the bitumens, coal, and charcoal. He found, that by digesting them with a sand heat in nitric acid, 100 grains being used to one ounce of acid of the specific gravity of 1.4, and fresh portions of the acid being added as it was decomposed or dissipated, a solution was obtained, in a few days, of a dark brown colour, which afforded, when evaporated to dryness, a substance having the general properties of tannin, and which precipitated solutions of gelatin. 100 grains of vegetable charcoal yield about 114 grains of this matter in a dry state.

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* Memoires d'Arcueil, tom. ii. p. 33.

† Annales de Chimie, tom. lxxxvii. p. 103. Philosophical Magazine, vol. xlv. p. 74.

This substance Mr Hatchet found was best obtained from carbonaceous matter, uncombined with any principle but oxygen; and hence substances frequently did not produce the tanning matter when treated with nitric acid, which, after having been charred, produced it copiously. Animal matter could thus be made to afford it by previous charring, and thus, as he remarked, "one portion of the skin of an animal might be made to convert another into leather †."

In conformity to this, too, substances charred by sulphuric acid, afforded artificial tannin when afterwards treated with nitric acid; and even in some cases, a portion of it appeared to be formed by the continued action of the sulphuric acid. This he afterwards investigated more fully, and found, that by digesting sulphuric acid on a number of resins, balsams, camphor, oil of turpentine, linseed oil, olive oil, and wax, washing the residuum, and

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* Nicholson's Journal, 8vo, vol. ii. p. 114.

† Philosophical Transactions, 1805, 1806.

digesting it in alkohol, tanning matter was procured. In a second series of experiments he discovered, that almost every vegetable substance might be made to afford tannin, by the repeated distillation of nitric acid from it without any previous charring. He thus procured it from resins, gum-resins, balsams, indigo, and several other varieties of vegetable matter; some affording it with more difficulty than others, or requiring more distillations of the acid, and affording it also in different quantities. Some gum-resins did not afford it, though, had the distillation been more frequently repeated, they probably might have done so. Gum arabic, gum tragacanth, and manna, afforded oxalic acid, but no tannin.

The nature of the product of all these operations was ascertained by the precipitate it gave with gelatin, and, in some cases, by skin being tanned by its operation. It resembled, too, in almost all its other properties, natural tannin. Its flavour was astringent: exposed to heat, it swelled, and gave a voluminous coal; it was speedily dissolved by cold water, and by alkohol. Its solution produced copious precipitates when added to solutions of muriate of tin, acetate of lead, and red sulphate of iron. It precipitated gold in its metallic state from its solution. With nitrate of lime, nitrate of barytes, and other earthy salts, it likewise gave precipitates. The alkalis deepened the colour of its solution, and then rendered it turbid. Sulphuric and muriatic acid throw down a copious brown precipitate, soluble in warm water, and capable of precipitating gelatin *.

The products of these processes, however, though all possessed of the essential characters of natural tannin, differ somewhat from it and from each other. Mr Hatchet remarked three varieties,—the first, produced by the action of nitric acid on any carbonaceous substance, vege-

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* Philosophical Transactions, 1805.

table, animal, or mineral; the second formed by distilling nitric acid from resins, balsams, and similar substances; and the third, extracted by alkohol from resins, camphor, &c. digested with sulphuric acid.

The first approaches nearest in its properties to natural tannin. It resembles it in its solubility in water and in alkohol; in its action on gelatin and on skin; in its effects on the metallic solutions, on the alkalis, and on the earths; and in the changes produced in it by sulphuric and muriatic acids. The only marked difference between them is in their relation to nitric acid. It owes its origin to the action of this acid, and is not changed by the continuance of that action. It suffers no alteration even when the acid is repeatedly distilled from it, while natural tannin is destroyed by the action of this acid; though some varieties of it resist it longer than others. The second variety, formed from resins, by the repeated action of nitric acid, favoured by heat, differs from the first principally in the precipitates which it forms with gelatin, which are always of a yellow colour, pale or deep, while those formed by the other are constantly brown. The third variety, produced by the action of sulphuric acid on resins, balsams, and similar substances, is inferior, in the energy of its action on gelatin and skin, to the first; it is converted into it, by the action of nitric acid. By the continuance of the action of sulphuric acid, it is decomposed and converted into coal.

The first variety of tannin afforded, when decomposed by heat, products analogous to those of animal matter. First a little water, with a small quantity of nitric acid, came over, then a small portion of a yellowish oil: on raising the heat, a large quantity of elastic fluid was disengaged, which was principally ammonia; and afterwards carbonic acid gas, with a little nitrogen. A bulky coal remained, which on incineration afforded a little lime.

From this analysis, a portion of acid appears to exist in these compounds. This acid can also be discovered in them by its sensible qualities. Mr Hatchet remarked their property of reddening litmus, and Dr Bostock found them, when prepared with every precaution, always to contain a portion of acid which cannot be removed from them. Thenard has regarded them as compounds of vegetable matter, with the acids employed in their formation,—an opinion conformable to his hypothesis, that natural tannin is a compound of this nature; and a similar supposition had been advanced by Chevreul, who instituted an extensive series of experiments on this subject [*]. The opinion is however vague, for it is not pointed out what species of vegetable matter is in combination with the acid; and though these artificial products may contain it, it is conformable to the changes of composition to which vegetable matter is liable, to suppose, that by the action of the acid employed in their formation, a decomposition of the substance operated on may be effected, and a new combination of its elements established.

From the facility with which some vegetable substances, after being charred, are converted into tannin, Mr Hatchet supposes, that some such method may be economically employed in practice. He accordingly found, that after extracting the tannin from oak bark, by repeated maceration in different portions of water, it acquired, by submitting it to the action of very dilute nitric acid, the property of precipitating gelatin, and this repeatedly. Peat, which consists of vegetable matter in a carbonized state, affords a large quantity of tannin, by such a process, with great facility; and the tanning quality of the water of peat moors, Mr Hatchet conjectures, may be derived from some spontaneous change of a similar nature [†].

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[*] Annales de Chimie, tom. lxx. lxxiii. Memoires d'Arcueil, tom. ii. p. 495. Nicholson's Journal, vol. xxxii. p. 360.

[†] Philosophical Transactions, 1806.

The art of tanning, or converting the skin of animals into leather, depends on the operation of the principle, the chemical history of which has now been given. It consists in combining tannin with the gelatin which is the basis of the skin; and all the manipulations of the art are directed to facilitate or effect this combination. A concise account of these, I take principally from a memoir by Davy on this subject *.

The skin requires to be prepared, by freeing it from the hair and other extraneous matter. This is done by washing it, and in some cases by inducing a slight degree of putrefaction, by which the epidermis is loosened, and the hair more easily detached. More generally it is effected by the action of lime; the lime being diffused in water, and the skin steeped in it; the lime combining with the cuticle, and forming a compound, which is loose and friable. The fat and oily matter form with the lime, too, saponaceous compounds, and are thus removed.

After the skin has been cleaned, it is submitted to other operations, before it is immersed in the tan liquor. According to Davy's account of the practices of the art, the large and thick hides which have undergone incipient putrefaction, are introduced for a short time into a strong infusion of oak bark, and after this they are acted on by water impregnated with a little sulphuric or acetic acid, in consequence of which they become harder and denser than before, and fitted, after being tanned, for the purpose of forming the stouter kinds of sole leather. The lighter skins, after having been subjected to the action of lime, are macerated in a ley formed from the infusion of pigeons dung in water, which contains a little carbonate of ammo-

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* Journals of the Royal Institution, vol. i.

nia; the hardness they had acquired from the lime is thus removed, and they become soft.

The tanning liquor is prepared by infusing bruised oak bark in water: and skins are tanned, by being successively immersed in these infusions, saturated in different degrees with the astringent principles of the bark. The first leys are weak, but towards the completion of the process, they are used as strong as possible; and in preparing stout sole leather, the skins are kept in an ooze, approaching to saturation, by means of layers of oak bark.

The infusion of oak bark, especially that obtained by the first maceration, contains principally tannin and extractive matter. In the course of the maceration of the skins in these liquors, the tannin combines gradually with the gelatin, which, in an organized form, is the basis of skin, and forms with it a compound insoluble in water, dense and impermeable to that fluid, while it possesses a certain degree of elasticity, and is not putrescible. The extractive matter also enters into the combination; for when skin in large quantity has exerted its full action on a small quantity of infusion, it abstracts the whole dissolved matter, and renders it colourless. From this extractive matter colour is derived, and the skin may perhaps be rendered more dense. The gallic acid was supposed by Seguin *, to facilitate the combination by de-oxidating the skin, but of this there is no proof; and the operation can be performed sufficiently, though this acid is not present in the tan liquor.

The operation of tanning requires a number of months, from the skins being successively and slowly introduced into infusions of different degrees of strength. Seguin, after his discovery of tannin, proposed to abridge the process, by introducing the skins more speedily into strong infusions of the tanning substance; and in this way, ac-

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* Nicholson's Journal, 4to, vol. i. p. 277.

cording to the report given on the art of tanning, by Peletier and Lelievre*, the whole could be finished in about twenty days, and leather obtained equal in quality to that prepared by the old method. There is reason, however, to doubt of the superiority of this new method. Mr Nicholson, in some observations on this subject, when a patent was taken out for Seguin's method in this country †, stated, that from information acquired from the manufacturers, he found that they had been sufficiently acquainted with the powers of the strong tanning infusions; and that these had been employed so as to abridge the process. But the leather thus prepared was not equal to that prepared in the old method. The advantage of the slow and gradual process appears to be, that the substance of the skin is penetrated, and equally changed: while in the more rapid method the external parts must be more acted on; and the texture probably will be more unequal. It appears also, from Davy's experiments, to combine with a larger quantity of the extractive matter contained in the astringent infusion; and hence the advantage of the immersions in the weak liquors, as these contain more of this than the strong infusions. It must be confessed, however, that for any thing theory can discover, the common process appears to be unnecessarily protracted, and some advantage might probably be derived from adopting some of the manipulations of Seguin.

The skin in tanning increases in weight, from the fixation of the vegetable matter: the quantity of this is from one-fifth to one-third of its weight. The increase is greater, according to Davy's experiments, from quick than from slow tanning. In the latter, he supposes more of the extractive matter enters into combination, and this weakening the attraction of the skin to tannin, less of it is absorbed, and thus less vegetable matter enters into the composition of the leather. Probably also, in the slow process, more of the animal matter is removed.

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* Memoires de Chimie de Pelletier, tom. ii. p. 557.

† Journal, 4to, vol. i. p. 26.

Other substances are used in tanning, as the bark of the willow, elm, and other trees, and even galls and catechu. The leather prepared from these varies in colour, and in some other external qualities.

Another application of tannin is in the composition of writing ink. This is formed from galls, frequently with an addition of logwood, and sulphate of iron, macerated in water; a quantity of gum-arabic is added to give consistence to the liquid, retard the subsidence of the colouring matter, and prevent it from flowing too quickly from the pen; a little sugar is sometimes added to give lustre. The black colour of ink depends on the joint action of the gallic acid and tannin on the oxide of iron, the compound they form of a deep colour being retained in suspension or solution by the action of the gallic acid, and the sulphuric acid of the salt. It is stated by Vauquelin and Deyeux, in a report on this subject *, that the nature of the combination constituting the colouring matter of ink, differs according as infusion or decoction of galls is employed. In infusion the gallic acid principally is dissolved with less of the tannin and extract; and the colour it produces with sulphate of iron has a shade of blue, becoming black on exposure to the air; in decoction all the soluble parts are taken up; and the colour produced with sulphate of iron is a deeper black with a shade of brown, and more sediment is deposited from this than from the other on keeping. Four ounces of galls pounded, and infused in a quart of water, one ounce of gum-arabic, and the same weight of sulphate of iron, (which ought to be calcined, to super-oxygenate it), give, they add, an ink which is

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* Nicholson's Journal, vol. xxix. p. 340.

light, fine, and of a purple tinge, becoming black on the paper. The addition of logwood renders the ink somewhat brown: it considerably deepens the colour, however, at little expence, and renders it more smooth and glossy; the boiling the galls and logwood in water has the same recommendation of economy, as the active matter is more completely extracted; and Bancroft supposes, that the colour is rendered more permanent. When galls alone are employed, the proportion of sulphate of iron of one to three is too large; but if logwood be added, even more, with an additional proportion of water, may be used. Dr Bancroft, in conformity to these observations, gives the following recipe: Twelve ounces of galls pounded, and six ounces of logwood, are to be boiled in successive portions of water, so as to form a gallon of decoction; and in this are to be dissolved five ounces of sulphate of iron, five ounces of gum-arabic, and two ounces of sugar *.

The vegetable matter in ink is liable to slow decomposition, probably from the continued action of the metallic oxide, and the sulphuric acid; hence the decay of ink by age, so that manuscripts at length become illegible. The oxide of iron, however, remains impressed on the paper, and hence the colour may be in some measure restored, by spreading over the paper a dilute infusion of galls, or, what is preferable as not colouring the paper, a solution of gallic acid; or, what is a more effectual mode, a blue colour may be produced, and the letters rendered visible, by a dilute solution of an alkaline prussiate. On this subject, some observations were made by Blagden †. Vauquelin and Deyeux remark, that the same method may be employed where the ink has been obliterated by oxymuriatic acid; if by oxalic acid, the prussiate will restore the writing of a reddish brown colour. The alkaline hydro-

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* Nicholson's Journal, vol. xxxvi. p. 2.

† Philosophical Transactions, vol. lxxvii. p. 451.

sulphurets are also powerful in restoring obliterated writing, producing a colour on the lines of a greenish black, or brownish red. Charcoal forms the best basis of an indestructible ink, and the easiest and best form of attaining this, according to Dr Bancroft, is simply the diffusion of fine lamp-black in oil of turpentine.

Tannin is the basis of the black dyes, these being obtained from sulphate of iron, acted on by infusion of galls, or other astringents.

Tannin, it has been supposed, as a test of gelatin, may sometimes afford information of importance in cases of morbid affection, as it can discover the presence of that principle, and even its quantity, in the secreted fluids.

SECT. XV.—OF INDIGO.

THIS substance, one of the principal dyeing materials, has been classed as a variety of what has been vaguely denominated Colouring Matter. It has properties, however, perfectly characteristic, and is obtained in a state sufficiently insulated and uniform to be entitled to be ranked as a distinct principle, is the produce of different species of the genus Indigofera, which are cultivated in America and the West Indies; and is in some measure an artificial preparation. The plant being cut, when ripe, is put into large troughs or vats, with water, and is pressed down. It undergoes a species of fermentation, and aërial matter is disengaged, partly inflammable, and said to be a mixture of carburetted hydrogen and carbonic acid. The water becomes turbid, from the formation or extraction of the colouring matter; and when the fermentative process is sufficiently advanced, it is drawn off into another vat, where it is kept constantly agitated, to promote the separation of the colouring particles, and the disengagement of a quantity of carbonic acid. Towards the end of this stage of the operation, a portion of lime-water is added, which farther favours the separation of the colouring matter. The liquor is withdrawn into another vessel, in which the deposition is allowed to go on: the clear liquor above, which is of a yellow colour, is drawn off: the thick sediment at the bottom is received into linen bags, through which the remaining fluid strains: the indigo remains in the state of a paste, which is dried by exposure to the air, excluding the solar rays. It differs in its qualities, according to the species of the plant, its state with regard to maturity, and the care with which the operation has been conducted. The rationale of the process is not well understood. The plant, by expression or infusion, affords only a green colouring matter previous to the fermentation; and we have no precise facts from which it can be determined, how this fermentation is so easily excited, or what are the changes connected with the production of the colouring matter. Some other plants yield indigo, and without requiring the same method. Dr Roxburgh, from a species of Nerium, to which he has given the distinctive appellation of Tinctorium, a native of Malabar, obtained indigo, merely by macerating the leaves in water at 160°, while by the usual process of fermentation none was obtained, and even by a slight fermentation it was destroyed. This indigo has all the properties of the other, and is of such a quality, that it is largely imported from India *.

Indigo is of a very rich blue colour, varying in its shade in different specimens. It is light and friable, has a smooth fracture, is tasteless, and has scarcely any perceptible smell. From Bergman's experiments it appears to be a heterogeneous substance, since besides its colouring matter he

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* Transactions of the Society of Arts, vol. xxviii.

found it to contain gum, resin, and earthy matter, and oxide of iron; the proportions in 100 parts being 12 of gum, 6 of resin, 22 of earthy matter soluble in acetous acid, 13 of oxide of iron soluble in muriatic acid, and 47 of pure colouring matter: but it is not easy to determine how far any of these is essential. Bergman was disposed to consider the iron as such, and as contributing to the colour; but, as Berthollet has remarked, the method he used to discover it led him to over-rate its quantity: and the greater part of what he did abstract by the action of muriatic acid, was removed without affecting the colouring matter.

Indigo exposed to a moderate heat emits vapours, and a purple-coloured substance sublimes, which, in close vessels, condenses in needle-like crystals. This Chevreul regards as pure indigo, free from the foreign matter present in common indigo. When again heated, it still rises in a purple vapour, and it dissolves in concentrated sulphuric acid, imparting a rich blue colour. It has been affirmed that this purple vapour, when exposed at its formation to quicksilver heated, forms an amalgam with it *.

When indigo is heated with the admission of the air, it burns slowly with a white flame.

Indigo yields to warm water extractive matter slightly bitter and astringent, of a yellowish brown colour: with this is dissolved greenish matter, which precipitates and becomes blue on exposure to the air, and which Chevreul, in his researches on this principle †, has considered as indigo at the minimum of oxidation. By the action of water, the inferior kinds of indigo, according to Quatromere, are improved in their quality, probably by the abstraction of mucilaginous and extractive parts. The colouring matter of indigo is equally insoluble in alkohol, and in ether,

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* Philosophical Magazine, vol. xlv. p. 396.

† Nicholson's Journal, vol. xxxii. p. 211.

a small portion of resin only being dissolved: according to Chevreul, however, it is partially dissolved, and afterwards precipitates.

The action of acids on indigo is more energetic. Concentrated sulphuric acid dissolves it in the cold: the solution appears black, from the deepness of its colour. It is this solution diluted with water that is known by the name of Liquid Blue, and that forms also the Saxon blue dye. Bergman found the colour to be changed to a green by a number of substances; as sulphurous acid, vinegar, ammonia, alkaline sulphurets, sulphate of iron, and sulphuretted hydrogen; and by some of these the colour was entirely destroyed. As all these might operate by abstracting oxygen, it appeared probable that it is to this operation that the change of colour is owing; yet there are other facts not easily reconciled with this, the blue being changed to a green, or being even destroyed, by other substances which cannot be supposed to exert any such agency, as by soda and potash, and black oxide of manganese. The acid in some states does not easily dissolve the indigo,—the addition of a little vegetable matter accelerates the solution.

The alkaline carbonates throw down from the solution of indigo in sulphuric acid, a blue powder, which Bergman named Precipitated Indigo.

Nitric acid decomposes indigo. The action, when the acid is concentrated, is so violent as to inflame it; and when diluted, it still acts on it with effervescence; the indigo becomes brown, and the residuum amounts only to the third of the original weight. A substance is formed, which remains in the state of a coagulum, which, freed from nitric acid by washing, forms a brown-coloured viscous mass, of a strong bitter taste, requiring a larger quantity of water for its solution, and more soluble in alkohol. This is the substance which has received the name of Bitter Principle *. A little oxalic acid is also formed; and from Hatchet's experiments it appears, that one of the varieties of artificial tannin is produced, the solution in water of the residual matter becoming turbid from the action of gelatin.

Muriatic acid does not act on the colouring matter of

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* This product has very peculiar characters, and has been repeatedly the subject of chemical experiment. It was first noticed by Haussman in his experiments on Indigo, (Journal de Physique, tom. xxxii. p. 161.). Welther observed its production in the action of nitric acid on silk, and from its bitterness gave it the name of AMER. Proust, Fourcroy, and Vauquelin, observed the formation of a similar product from the action of the same acid on the muscular fibre and other animal solids. Chevreul has given the following process for its formation, (Nicholson's Journal, vol. xxx. p. 350.): Two parts of indigo are submitted to the action of four parts of nitric acid, diluted with four of water, a moderate sand heat being applied: nitric oxide and carbonic acid gases are disengaged; and prussic acid with nitric acid distil over: the action becomes violent; it is then moderated by removing the vessel into cold water, where it is left for twenty-four hours. A liquor remains in the retort of a reddish colour; and two concrete substances float in it, one of a resinous appearance, the other of an orange yellow colour. The liquor poured off and concentrated by evaporation deposites on cooling crystals of *amer*, and of an acid substance. These being dissolved in hot water, the acid retaining a little amer in combination is deposited on cooling; and by farther evaporation the amer is obtained in yellow scales: this yellow colour is derived from a little resin, and there also adheres to it a little of the crystallized acid. When sufficiently purified, it is of a white inclining to straw colour; it sublimes from the application of a gentle heat, and condenses in needles or scales: it is inflammable; exposed to a red heat it affords nitrous, prussic, and carbonic acids, nitric oxide, nitrogen, carbonic oxide, and olefiant gases, and a little charcoal remains. It is more soluble in hot than in cold water; its solution is acid and bitter. When

indigo, but dissolves merely the oxide of iron, and the earthy matter it contains. It dissolves, however, a portion of what Bergman calls Precipitated Indigo, and acquires a deep blue colour. A number of the other acids, as the phosphoric, acetic, and tartaric, act on it in the same manner as the muriatic: so that no acid, properly speaking,

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mixed with a concentrated solution of potash, small needle-like crystals of a gold colour are formed, which are a compound of amer and potash. This compound, which had been examined by Welther, and by Fourcroy and Vauquelin, has the property of detonating when heated, forming prussic acid in the detonation: it is decomposed by nitric or muriatic acid at a boiling heat, and on cooling, amer crystallizes. The compound of amer with ammonia, scarcely detonates on being heated: With the alkaline earths it unites and forms compounds soluble in water: it also dissolves the oxides of silver, quicksilver, and lead; and all these compounds detonate when heated. Chevreul supposes the amer to be a compound of nitric acid with vegetable matter; these detonations he ascribes to the reaction of the acid, and particularly of its oxygen at a high temperature on the elements of the vegetable matter, whence the abundant and rapid formation of elastic products; and the detonation is more especially observed in its combinations with the alkaline bases or metallic oxides, as these render it fixed, and thus subject it to the action of a higher temperature.

The formation of this product in the action of nitric acid on animal matter is afterwards to be considered. The acid formed with it, resembles it in the greater number of its properties, and is regarded by Chevreul as a similar compound with an inferior proportion of nitric acid, amer being formed by boiling it with nitric acid. It combines with the alkalis, earths, and metallic oxides, but its compounds do not detonate when heated. There is alongst with it a formation of one of the varieties of artificial tannin, which Chevreul considers also as a compound of resin, amer, and nitric acid, (Nicholson's Journal, vol. xxxii. p. 360.)

dissolves this substance directly but the sulphuric. Oxymuriatic acid destroys its blue colour, when the indigo is in a state of solution.

The fixed alkalis dissolve some of the substances contained in indigo, but not its colouring matter. The precipitate from the solution of indigo in sulphuric acid, is dissolved by them easily even in the cold : the blue colour gradually changes to a green, and is at length destroyed. With the alkaline carbonates the same solution is effected, but the colour is not altered. The action of ammonia and of lime is the same with that of the pure fixed alkalis.

Indigo subjected to destructive distillation, is decomposed : it leaves a residue of 33 parts from 100, consisting of earthy matter and oxide of iron ; of the remaining 67 parts, it appears from the preceding analysis by Bergman, that 47 is the pure colouring matter; the products from this he found to consist of carbonic acid 2 parts, alkaline liquor (composed of carbonate of ammonia dissolved in water) 8 parts, empyreumatic oil 9 parts, and 23 of charcoal, which, burnt in the open air, left 4 parts, about half of which was oxide of iron, and the other half appeared to be siliceous earth : hydro-sulphuret of ammonia and prussiate of ammonia are also disengaged, according to Chevreul. From this analysis it may be inferred, that the colouring matter of indigo consists of hydrogen, oxygen, nitrogen, and carbon, with perhaps a little sulphur, the proportion of carbon being unusually large, and such, indeed, as scarcely appears to be contained in any other vegetable principle.

The chemical properties of this substance are evidently different from those of any other vegetable principle. The application of it to dyeing presents some singular phenomena; for although it is not soluble in alkaline solutions or in lime, yet, by the intervention of other substances, this solution is effected, so as to form a dye-liquor.

Bergman examined two of the processes of the dyers, One consists in mixing indigo with an equal weight of sulphate of iron, and twice its weight of lime, and boiling them in water; the indigo soon dissolves. In the other, a solution of pure fixed alkali is taken, and to this indigo, and orpiment or sulphuret of arsenic, are added: the indigo is dissolved, and the bath becomes green. Bergman supposed, that the sulphate of iron in the one process, the sulphuret of arsenic in the other, operates by communicating phlogiston to the indigo, in other words, by abstracting from it oxygen; and this appears to be confirmed by the facts he ascertained, that if the sulphate of iron has been previously boiled some hours in water, in which case it becomes more oxidated, it does not promote the solution of the indigo, and that oxide of arsenic is also equally unfit for this purpose. Haussman in some measure established this theory, by proving, that a solution of sulphuret of arsenic mixed with indigo absorbs oxygen; and the indigo is reproduced with its blue colour, and precipitated. This was confirmed by Berthollet, who farther observed, that when cloth is dyed in the indigo liquors prepared by these processes, it is of a green colour, but becomes blue by exposure to the air; and he found, that a piece of cloth, coming out of the vat of a green colour, became blue by dipping it quickly in oxymuriatic acid. He concludes, from these facts, that indigo, in its natural state, contains oxygen, which may be abstracted from it; it then becomes green; in this state, it is soluble in solutions of the alkalis, and of lime; it is again capable of attracting oxygen, when it acquires the blue colour, and precipitates. When dissolved by sulphuric acid, it is not deprived of oxygen, and therefore retains its blue colour, which the cloth at once acquires; yet, even in this solution, the indigo, as Berthollet remarks, appears to have suffered a slight deoxidation, and to this he ascribes the solubility in alkalis of the precipitate thrown down from this solution.

Woad is a substance produced by a process similar to that followed in extracting indigo, and bears some resemblance to it. It is extracted from the Isatis tinctoria and Isatis Lusitanica. The plant is cut down, washed, and dried in the sun: it is ground in a mill, and reduced to a paste. Of this heaps are formed, which are covered to secure them from rain. This paste, after having remained for a fortnight, is turned, and its different parts mixed: it is then made into balls, which are deprived of their moisture by exposure to the air and sun. These balls, heaped together, gradually become hot, and exhale an ammoniacal odour; the heat is increased by watering the heap slightly until they are reduced to a coarse powder. In this state woad is used; it gives a blue colour, which is permanent, but has not the beauty of that from indigo. If the plant, however, be subjected to the same processes that are followed in preparing indigo, it affords a colouring matter precisely the same *; and there can be little doubt, therefore, that the colouring matter of woad is indigo. It affords, according to Chevreul, the same products in its decomposition by heat, and indigo may be extracted from it by the action of alkohol.

Sect. XVI.—OF ULMIN.

This is a peculiar vegetable product, which was first obtained as an exudation from the bark of the elm by Vauquelin, and was afterwards more fully noticed by Klaproth. Vauquelin found it to consist, in its natural state, of potash, with a matter similar in some of its properties to gum. And Mr Smithson, from experiments upon it,

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* Berthollet on Dyeing, vol. ii. p. 72.

inferred, that it is a compound of potash with a matter which, " if not of a peculiar genus, seems rather more related to the extractives than to the resins." Dr Thomson, who had considered it as a distinct principle, and given it the name of Ulmin, has since procured it free from potash. It has also been found to be a product of other trees, as the oak, hornbeam, and horse chesnut; and, according to Berzelius, it is a constituent ingredient even of the greater number of barks.

Ulmin in its usual state combined with potash, and, forming an exudation from the bark of the elm, is in small masses, of a dark brown or black colour, with a resinous lustre and fracture; it is nearly tasteless, or has only a slight astringency; it dissolves easily in the mouth; it swells when heated, but does not melt; it burns at the flame of a candle, and is consumed, leaving carbonate of potash; it dissolves readily in water, forming a solution of a dark reddish brown colour, and yellow when dilute, which, even when much concentrated, is not slimy or mucilaginous: it is insoluble in alkohol or ether, and it is partially precipitated from its watery solution by alkohol. Nitric, muriatic, and sulphuric acids, throw down a reddish or yellowish-brown precipitate; acetic acid does not precipitate it; no effect is produced on the solution by infusion of galls, or by animal gelatin; sulphate of iron throws down a brown precipitate, and precipitates are formed by some other metallic salts, generally of a similar colour. The simplest analysis of this substance is by the addition of an acid to its solution. The peculiar vegetable matter which is its basis is precipitated, and the salt formed by the combination of potash with the acid which has been added remains, with a portion of the vegetable matter in solution. The potash it contains is also obtained by calcination or combustion. From 20 grains, Dr Thomson obtained by calcination 3.8 sub-carbonate of potash, with 1 of carbonate of lime, and 0.2 of silex and oxide of iron, the two latter being probably accidental. Mr Smithson inferred, that the quantity of potash amounts to about 1-5th of the natural product. The alkali seems to be in very intimate combination with the vegetable matter, as the compound does not affect the vegetable colours.

The vegetable matter which is precipitated from the watery solution of the natural product by the action of acids, and which may be regarded as the pure ulmin, is possessed of the following properties. It is in masses of a black colour, but in minute fragments is red and transparent, and has a highly resinous lustre and appearance. It is inflammable, burns with flame, and leaves white ashes. Alkohol dissolves it, but in very small quantity. Water likewise dissolves it, but also only in small quantity; the greater solubility, therefore, of the natural product is owing to the action of the potash it contains; and accordingly, on adding a little potash to water in which the precipitated ulmin lies undissolved, it dissolves immediately and abundantly, and the solution has all the properties of the native product: it is singular, however, that neither ammonia, nor carbonate of soda, promotes its solution. It appears to redden litmus paper. Acids cause its precipitation from its watery solution, though it appears to contain previously no alkali, and to retain none of the acid by which it is precipitated in combination.

Dr Thomson has obtained natural ulmin free from potash. It had been collected on an oak; and was in small masses of a dark brown colour, nearly black, firmer and of a greater specific gravity than the alkaline compound. It is nearly tasteless; dissolves very slowly, and in small quantity, both in water and alkohol; the solution is pale brown. The aqueous solution is not precipitated by sulphate of iron, copper or zinc, or by nitrate of silver; nitrate of mercury and super-acetate of lead occasion brown flaky precipitates. Acids do not precipitate it from its watery solution; in this respect it differs remarkably from the ulmin which is precipitated from the alkali naturally combined with it, by an acid. A weak solution of carbonate of potash poured upon it dissolves it readily, forming a dark brown solution, which has all the properties of the native compound with potash. It is this strong affinity to carbonate of potash, and its solubility from this combination, that forms the most characteristic property of ulmin. Calcined it leaves a white ash, amounting to 0.27 grain from 5 grains, which contained no perceptible portion of alkali, but was wholly carbonate of lime.

The ulmin naturally combined with potash, obtained from other trees, is similar in general properties to that from the elm. That from the oak has a taste more astringent and bitter, probably from intermixture of the astringent principle of oak bark; it does not, however, give any precipitate with gelatin, but it affords precipitates from some of the metallic salts, which differ in colour from those by the ulmin of the elm; in particular, that with sulphate of zinc is nearly black. Similar differences exist in the ulmin from the horse-chesnut, and it is not precipitated from its watery solution by acids, apparently from containing less potash, so that less of it exists in solution.

The method given by Berzelius to discover ulmin existing as a constituent ingredient of barks, is first to macerate the bark in alkohol, and afterwards in cold water; the tannin is thus abstracted, which otherwise combines with the ulmin, and prevents it from being recognized: the ulmin remains undissolved, and may be obtained by infusion in hot water, especially if a little carbonate of potash be dissolved in the water *.

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* Annales de Chimie, tom. xxi. Annals of Philosophy, vol. i. & ii. Philosophical Transactions, 1813.

SECT. XVII.—OF CINCHONIN.

A PRINCIPLE exists in some vegetables which has the property of forming with tannin an insoluble magma or precipitate, similar to that which tannin forms with animal gelatin. Dr Maton appears first to have observed, that infusion of Peruvian bark forms a precipitate with solution of tannin. Seguin supposed, that the febrifuge quality of the bark resides in this principle; and on the supposition of its identity with animal gelatin, he with much confidence recommended animal glue as a substitute *. Some experiments were made on this principle by Dr Duncan *junior*. He found, that except in combining with tannin, and forming a compound sparingly soluble in water, it is in no property analogous to gelatin. Its solution has no tendency to assume a gelatinous consistence; and it is not precipitated as animal gelatin is, by carbonate of potash. It is also soluble in alkohol, while gelatin is precipitated by alkohol from its watery solution. And it does not even separate from a watery solution of tannin, all that is precipitable by a solution of gelatin. He proposed to distinguish it by the name of Cinchonin †. Vauquelin, in his analysis of the various species of cinchona, found, that there are some which contain none of this principle, and which are not inferior to the others in medicinal power ‡. A dissertation has since been published by Dr Gomes ||, in which are some experimental results with re-

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* Nicholson's Journal, vol. vi. p. 136. † Ibid. p. 225.

‡ Philosophical Magazine, vol. xxvii. p. 36. 133.

|| Memoirs of the Academy of Sciences at Lisbon; or Edinburgh Medical Journal, vol. vii.

gard to its properties. The process he employed to procure it insulated, consisted in evaporating tincture of Peruvian bark to the consistence of an extract, adding to this successively small portions of distilled water while any colour or taste is acquired: filtering these solutions, then evaporating them; and adding to the solid matter successive portions of a solution of potash, until these come off colourless. A white substance is thus obtained, which is washed with a small portion of cold water. When dry it forms a powder, which is nearly pure cinchonin. By dissolving this in alkohol, straining the solution, adding to it an equal quantity of distilled water, leaving it exposed to the air until the alkohol evaporates, straining the residual liquor, and allowing the solid deposite to dry on the filtre, the cinchonin is obtained in fine white filiform crystals. These are described as insipid and inodorous, inflammable, insoluble in water cold or warm, soluble in alkohol, ether, and in acids, and yielding a precipitate from solutions in acids, on the addition of infusion of galls, which is redissolved by alkohol. This principle, as Gomes remarks, is analogous to resin in its inflammability, insolubility in water, and solubility in alkohol and ether; but it differs by its crystallization, and its solubility in acids. In these, as well as in the other properties, it bears a more close resemblance to camphor; but it differs from it in want of odour, in greater specific gravity, as it sinks in water, and in giving a precipitate with infusion of galls.

Some experiments have been also made with regard to it by Van Smissien, under the direction of Pfaff, the results of which nearly correspond with these, except that the crystals were found to be soluble in six times their weight of boiling water, and insoluble in ether: they were also found to be dissolved by caustic potash, and to be precipitated from this solution unaltered by sulphuric acid: their solution in alkohol did not affect the tincture of galls, and scarcely altered the solution of isinglass, but it gave a precipitate of a dark green colour with solution of sulphate of iron. The property of Peruvian bark, of its infusion forming a precipitate with infusion of galls, is supposed, from these results, to depend on the presence of another principle, analogous to extract; and the power which it has in some of its varieties of precipitating gelatin, is supposed to arise from that modification of tannin which precipitates iron of a green colour *.

SECT. XVIII.—OF EMETIN.

THIS is a principle which has been lately described by Magendie and Pelletier, as obtained by them from the root of ipecacuanha, and being apparently the matter in which its emetic power resides.

If ipecacuanha be digested with sulphuric ether, an oily odorous substance is dissolved, and can be procured by evaporation. If after this the ipecacuanha be digested in alkohol, on evaporating this tincture to dryness, a portion of solid matter is obtained; and when water is digested on this, it affords by evaporation emetin nearly pure, or with a trace only of gallic acid, which may be abstracted by maceration on carbonate of barytes. Or if to the aqueous solution of the residue from the evaporation of the spirituous infusion, a solution of acetate of lead be added, the emetin is precipitated in combination with the oxide of lead. The precipitate after being washed may be diffused in water, and a current of sulphuretted hydrogen gas transmitted through the liquor; the oxide of lead is precipitated by the sulphuretted hydrogen, and the emetin remains in solution. By evaporation it is obtained in scales, transparent, and of a brownish red colour.

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* Annals of Philosophy, vol. vii. p. 47.

This substance is inodorous; its taste is bitter, and somewhat acrid. It remains unchanged at the heat of boiling water; at a higher heat, without melting, it swells, becomes black, and is decomposed, affording water, carbonic acid, a small portion of oil and acetic acid, and leaving a spongy charcoal. No nitrogen is discovered in the products: it appears, therefore, to be a ternary compound of carbon, hydrogen, and oxygen.

It suffers no change from the air, farther than a slight deliquescence in a humid atmosphere. It is abundantly soluble in water, but does not crystallize from the solution; it is dissolved by alkohol, but not by sulphuric ether. Sulphuric acid decomposes and chars it. Nitric acid dissolves it, forming a red coloured solution, which becomes yellow; and after a disengagement of nitric oxide gas, yields crystals of oxalic acid. Muriatic, acetic, and phosphoric acids dissolve it, and afford it again, apparently without alteration, when saturated by an alkali. Gallic acid throws it down in a state of combination from its aqueous or spirituous solution; and this compound is dissolved by the alkalis. Nitrate of mercury, and corrosive muriate of mercury, cause precipitates from its solution. The other vegetable principles, and the animal principles, scarcely exert any action on it.

This substance is powerfully emetic; and in so small a dose as that of a grain or two, it occasions violent vomiting. This is one of its most characteristic properties; its chemical properties seem not to be very distinctive *.

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* Annales de Chimie et Physique, tom. iv. Annals of Philosophy, vol. x. and xi.

SECT. XIX.—OF GALLIC ACID.

THERE exists in the juices of many vegetables, at certain states of maturity, compounds possessed of acid properties: such acids are likewise found combined with some of the proximate vegetable principles; or united with the alkalis or earths, forming what have been named the Essential Salts of Plants. These native vegetable acids have been classed together, as they have a resemblance in acidity, and in chemical composition. They are not, however, to be regarded as mere varieties of a species: each forms a species, or peculiar proximate principle, with differences as important as exist among the other immediate principles of plants. Eight acids of this kind have been distinguished,—the Gallic, Citric, Malic, Oxalic, Tartaric, Benzoic, Acetic, and Prussic. To these some others have been added, as the Moroxylic and Sorbic, more doubtful or imperfectly defined.

The greater number of these acids are of similar composition with regard to their constituent elements; they are composed of carbon, hydrogen, and oxygen, differing only in the proportions; hence, by partial change of composition, they are convertible into each other; by oxygenation, in particular, they pass ultimately into the oxalic; and by decomposition by heat they afford the acetic, with carbonic acid.

In conformity to the theory of Lavoisier, that oxygen is the principle of acidity, these acids were supposed to consist of a compound radical of carbon and hydrogen, acidified by oxygen, and the distinctions between them were supposed to depend principally on the proportions of the elements constituting the radical. Nor was any other view presented in their more recent analysis by Gay Lussac and Thenard. These chemists considered them as ternary compounds, in which the oxygen is in excess. In conformity to the doctrine of acidity which I have illustrated in the preceding volumes, I consider these acids as compounds of a simple radical, carbon, with oxygen and hydrogen. Carbonic acid is the binary compound of carbon with oxygen, in which, in conformity to the principle suggested by this doctrine, the acidity is weak;—the different vegetable acids are the ternary compounds of carbon with oxygen and hydrogen, in which, conformable to the same principle, the degrees of acidity are much more powerful.

Under this view of their composition, it became of importance to determine the proportions of their elements, according to this relation. They have within these few years been submitted to analysis by Gay Lussac and Thenard, and by Berzelius; but the results are in general extremely discordant, as is apparent in the tables of the composition of the vegetable principles by these chemists, inserted pages 78. 79. But this discordance, as I have remarked in the observations on these tables, is more apparent than real. It arises from the point of view under which the composition is regarded. Gay Lussac submitted them to analysis in the driest state in which they can be procured, without the abstraction of what is considered as water of composition,—generally in combination with lime, in which they exist in this state. Berzelius, on the other hand, in conformity to the view which has been more recently universally admitted by chemists, that the greater number of acids contain water in combination, which it is necessary to abstract in determining their real composition, submitted them to analysis in this mode, by operating on them in the state of oxalate of lead, a combination in which this combined water is removed. But this view of the subject is incorrect; the water which is obtained in the action of oxide of lead on these acids, is not water which previously existed in their composition, but is water formed by the combination of portions of their oxygen and hydrogen. These, therefore, are to be admitted in the just estimate of their composition; and when this is done, the results of Berzelius coincide, as I have already remarked, in a striking manner with those of Gay Lussac.

The proportions of the elements of the principal vegetable acids, considered in conformity to the principle I have stated, afford a striking illustration of the theory, and a proof of its truth. Considering the oxygen and hydrogen as elements bearing a relation to the carbon as the radical or base of the composition, they are found to be in the usual definite proportions which they bear to it in their binary combinations, or in what may justly be considered as multiples or sub-multiples of these. Oxalic acid is carbon, with oxygen in the proportion which constitutes carbonic acid, and with hydrogen in its first or lowest proportion. Tartaric acid is carbon, with oxygen in the same proportion, and with hydrogen in its third definite proportion, or multiple. Acetic acid is carbon, with oxygen in its second proportion, or that which forms carbonic oxide, and with hydrogen in its second proportion, that which constitutes olefiant gas. Citric acid is carbon, with oxygen in the third definite proportion, that intermediate between carbonic oxide and carbonic acid, and with hydrogen in its first proportion. These results, and those with regard to the other vegetable acids, so far as they are established by analysis, will be more fully stated under their individual history.

I proceed first to the history of Gallic Acid, as it in some measure forms the transition from tannin, a principle with which it has an intimate connection. They generally exist together; either of them is seldom found in any vegetable without a portion of the other, and it is not certain if gallic acid has been obtained free from tannin.

This acid exists in largest quantity in the gall nut, whence it has received its name. The infusion of galls, it had been observed by the Dijon Academicians, reddens the infusion of litmus: they farther found, that the liquor obtained by distillation, strikes a black colour with salts of iron; and that its solution in water precipitates the alkaline sulphurets, and decomposes metallic solutions *. Scheele first obtained the acid in an insulated form, and described its properties. He observed, that an infusion of galls deposited a sediment of a grey colour, and of a crystalline appearance, which had an acid taste, and which precipitated sulphate of iron black. To investigate its nature, he allowed a strong infusion of galls to remain in a vessel imperfectly closed for some months. A thick mould was formed on its surface; its astringent taste diminished, and its sourness increased: a sediment was at length collected: this was washed with cold water, and then as much boiling water poured on it as was sufficient to dissolve it. On evaporating the filtered solution by a gentle heat, a salt was obtained, partly in the form of a fine sand, and partly in the form of radiated crystals, of a grey colour. This has been regarded as Gallic Acid †.

Other methods have been employed to obtain it. Scheele observed, that when galls are distilled with a strong heat, an acid liquor passes over, and afterwards a saline matter rises, having the properties of gallic acid. This method has been employed by Deyeux. At first a limpid fluid condenses, and afterwards crystals of a white colour form in the upper part of the vessel: the heat is stopt when the crystals towards the lower part begin to melt, as, if con-

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* Elemens de Chimie, tom. iii.

† Crell's Chemical Journal, vol. i. p. 24.

tinued longer, a portion of oil is volatilized, and renders them impure. Another method is, to boil carbonate of barytes with an infusion of gall nut; this affords a bluish green liquor, which appears, from the common tests, to contain neither tannin nor extract: when diluted sulphuric acid is dropt into it, it becomes turbid; sulphate of barytes is precipitated; and, after filtration, if the saturation of the earth be perfect, a colourless solution is obtained *. Fiedler employed the affinity of alumina, to abstract the tannin and extract from the gallic acid of the infusion of galls, boiling an ounce of galls in sixteen ounces of water, until half the quantity of liquid is evarated; and adding to this the quantity of alumina obtained from the decomposition of two ounces of alum by an alkaline solution, agitating them frequently: after twenty-four hours, the liquor being filtered, passes colourless; and it is not rendered turbid by solution of gelatin. This liquor being concentrated by evaporation, affords gallic acid in acicular crystals †. The process of Richter is to evaporate an infusion of galls in cold water to dryness, and to pour pure alkohol on the dry matter: it dissolves the gallic acid, and leaves the tannin undissolved: the alkohol is distilled from the solution to nearly a solid mass. Water is added to this, and a gentle heat applied. A solution, clear and almost colourless, is obtained, which, by evaporation, affords small white prismatic crystals of gallic acid, about half an ounce being obtained from a pound of galls ‡. Berzelius has combined the method by spontaneous decomposition of infusion of galls and sublimation. He renders the crystals deposited from the infusion as pure as possible, by a second crystallization from their watery solution; he then submits them to a moderate heat

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* Journals of the Royal Institution, vol. i. p. 274.

† Nicholson's Journal, 8vo, vol. i. p. 237.

‡ Philosophical Magazine, vol. xxiii. p. 74.

in a retort; they at first give out water, and then sublime, leaving a blackish brown mass, in which the presence of tannin may be recognized.

It is doubtful, whether, by any of these processes, gallic acid is obtained free from other principles. As obtained by the first process, it always retains a portion of tannin. Berthollet endeavoured to abstract this by the action of oxide of tin, and Proust employed muriate of tin for the same purpose, dropping it into the solution of the acid, while any flocculi precipitate, and evaporating the filtered liquor, till on cooling it afforded crystals *. But Lagrange found by experiment, that, if a small quantity of oxide of tin were employed, the tannin is not completely abstracted; and if a larger quantity were used, the gallic acid, as well as the tannin, is decomposed; the filtered solution neither precipitating gelatin nor sulphate of iron, and affording no gallic acid by evaporation †. The process of Fiedler, in which the affinity of alumina is employed to abstract the tannin, Davy found to be deficient; the filtered liquor, after the alumina had acted on it in the cold, gave a slight precipitate with gelatin; while, if it were boiled with it, the gallic acid itself was abstracted. The action of barytes is probably liable to the same difficulty. The method of Richter was found by Lagrange not to succeed, the acid either not being purified from the tannin, or being decomposed. There remains only the process by sublimation; and it is still to be determined, whether the product it affords is pure gallic acid.

Lagrange has compared it with the crystallized acid obtained by the process by Scheele. The latter he found imparted to water a slight lemon colour, which becomes deeper by the action of the air; it reddens infusion of litmus; lime water and barytic water produce in it a blue

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* Journal de Physique, tom. lxi. p. 107.

† Nicholson's Journal, vol. xvii. p. 62.

colour. Potash changes it to a deep brown, and ammonia to a reddish brown. With green sulphate of iron it gives a violet blue; with nitrate of mercury a yellow precipitate; with acetate of lead and muriate of tin, one that is white. It gives a copious precipitate with glue. With the acid prepared by Richter's process, the results from these re-agents were similar.

The *sublimed acid*, Lagrange found, when dissolved in water, to emit an aromatic odour, and a slight oily pellicle appeared on its surface. Its solution becomes brown on exposure to the air; it faintly reddens infusion of litmus; lime-water in excess, and barytes, give it a fawn colour: potash and ammonia render it brown. Sulphate of iron dropt into it produces a blue colour, which soon changes to a violet; sometimes the colour, instead of being blue, is a deep green, apparently from the degree of oxidation of the metal; and from the action of muriate of iron it is always so. With nitrate of mercury the precipitate is blackish; with acetate of lead it is fawn-coloured; muriate of tin produces no change. It does not precipitate glue*.

From these results, the sublimed acid appears to be free from tannin, but to contain a small portion of volatile oil, whence the odour of its solution, and probably some of the phenomena displayed in the effects of re-agents upon it. The crystallized acid obviously contains tannin, whence it precipitates gelatin abundantly, and to this some of its other properties may be ascribed. It appears also to be more powerfully acid, which may be owing to a portion of some other vegetable acid (the acetic, as Lagrange conjectures) adhering to it. The sublimed acid may therefore be regarded as that which approaches nearest to purity; though it is also possible, that by the process of sublimation it may have suffered some change. From some farther experiments, Lagrange advanced the opinion, that the gallic acid obtained by Scheele's process is a compound of acetic acid with tannin and extractive matter; and the sublimed acid the acetic combined with less of these principles, and having united with it a little volatile oil. The only proofs given of this opinion are, that on distilling galls either with or without water, an acid liquid was obtained, which, when saturated with potash, gave indications of acetic acid; and acetic acid was also afforded from the decomposition by heat of the alkaline and earthy gallates,—results which might arise from a formation of acetic acid in the decomposition. It is also improbable that acetic acid, by combination with tannin or extract, should acquire the property of crystallizing; and the probability has been already stated of the opinion, that tannin is rather a combination of gallic acid, than gallic acid of tannin.

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* Nicholson's Journal, vol. xvii. p. 64.

The sublimed acid in its purest state is of a white colour, and crystallizes in slender prisms; its taste is sour, and its solution reddens the vegetable colours; according to Berzelius, however, its taste is only bitter, and it does not redden litmus. It excites effervescence with the alkaline carbonates, but does not decompose the earthy carbonates. It is soluble, according to Scheele's experiments, in its weight and a half of boiling water: the solution as it cools becomes turbid, from the formation of small crystals; it requires 24 parts of cold water to dissolve it. It is more soluble in alkohol: dissolving in its own weight when the alkohol is boiling, and requiring about four parts when cold.

When exposed to heat, it fuses, giving an agreeable odour, and leaving a hard coal, which is with difficulty reduced to ashes. When the operation is performed in a retort, an acid liquor comes over, without any oil; and a portion of it sublimes, remaining fluid while the neck of the retort is hot, but shooting into crystals as it cools. A large quantity of charcoal remains in the retort. From the products of its analysis, Berzelius has stated its composition at hydrogen 5.00, carbon 56.64, and oxygen 38.36 *. But this, in conformity to his views, is the composition of the acid free from combined water, such as he supposes it to exist in certain combinations,—that, for example, with oxide of lead, the state in which he operated on it. To give the real composition, conformable to the theory I have illustrated, the proportions of oxygen and hydrogen of this combined water must be added to the others. The quantity is most directly determined on the principle which has likewise been illustrated, that the quantity of oxygen expended in the formation of this water, will be equivalent to the quantity of oxygen in the oxide which the acid saturates. Berzelius found, that 100 of what he considers real gallic acid, saturate a quantity of base containing 12.44 of oxygen; the hydrogen equivalent to this is 1.5; hence these added to the above proportions, give as the composition carbon 56.64, oxygen 50.8, hydrogen 6.5. This gives the proportion of oxygen to carbon less than that which constitutes carbonic oxide; and if the oxygen in the latter be considered as the second multiple, that in gallic acid will be almost exactly the mean between it and the first. Considering the hydrogen in super-carburetted hydrogen as the second proportion or multiple of that element, the proportion in gallic acid is nearly the first.

This acid combines with the alkalis and earths, forming salts denominated Gallates, the properties of which have been little examined. Richter has remarked, that the alkaline gallates form black precipitates with solutions of iron, and likewise precipitate all other metallic solutions. Lagrange has stated, that they scarcely precipitate glue, even when the acid from which they are formed precipitates it copiously, owing no doubt to the tannin which is present being retained in combination with the saline matter. The alkaline gallates have a considerable degree of

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* Annals of Philosophy, vol. v. p. 176.

solubility; they have often a green colour, probably from impregnation of foreign matter.

Scheele remarked, that gallic acid precipitates metals from their solutions of different colours; and he added several facts with regard to these precipitations, which, however, are of less value, as the acid he employed must have contained tannin. Its solution gives a dark green colour to a solution of gold, and a brown powder is gradually deposited, which is gold revived. A solution of silver is rendered brown, and deposites, if warm, a grey powder, which is silver in its metallic state. A solution of mercury is precipitated of an orange yellow. A solution of copper yields a brown sediment. Acetated lead is precipitated white. Bismuth gives a lemon-coloured precipitate. The acid of molybdena becomes of a dark yellow, without any precipitation. Platina, zinc, the acid of arsenic, tin, cobalt, and the regulus of manganese, undergo no change *.

Gallic acid gives a black, or rather a very deep blue colour, with the salts of iron: the precipitate on which this depends is, as Proust has remarked, of greater tenuity, and remains longer suspended than that from tannin. In this action, the gallic acid appears to have nearly the same relation to the oxide that tannin has; producing the dark colour with the solution in which the iron is highly oxidated, while colour is scarcely apparent when the iron is at the minimum of oxidation, and this apparently from the same cause, the weaker affinity exerted by the acid of the salt to the oxide in its former state. Richter has maintained, that when a solution of gallic acid immediately forms a black precipitate in neutral solutions of iron, it is not pure, but contains tannin, which combines with the sulphuric acid, and separates from it the oxide of iron, which then combines with the gallic acid †. And it has

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* Crell's Chemical Journal, vol. i. p. 28.

† Philosophical Magazine, vol. xxiii. p. 75.

even been supposed, that the colour which this acid produces with the salts of iron, may in all cases be owing to a portion of tannin combined with it, and that the acid, by its re-action on the precipitate, only brings the compound more nearly to a state of solution.

According to Proust, gallic acid dissolves tannin, or rather renders it more soluble in water. Partly from this, and partly from both principles forming compounds with oxide of iron of a black colour, arises the advantage derived from their combination in the formation of inks and black dyes, or the superiority of an infusion of a vegetable astringent containing both, as the gall nut, to the use of either in a purer state. These applications, which only partly depend on the agency of gallic acid, have been already taken notice of under the history of tannin.

SECT. XX.—OF MALIC ACID.

SCHEELE, in examining the acid juices of unripe fruits, found that they consisted of two acids, in different proportions; one, which, being abundant in the fruit of the lemon, he named Acid of Lemon, and to which the name of Citric Acid has since been given; the other, which, from composing principally the juice of unripe apples, he named Acid of Apple, and which has since received the appellation of Malic Acid. The fruit of the gooseberry, of currants, bilberries, cherries, strawberries, and raspberries, contain nearly equal quantities of both acids: cranberries, whortleberries, birdcherries, and doghips, contain the citric, with little of the malic acid; while the juice of the barberry, elderberry, sloe, and plumb, consists of the malic acid, with little or no traces of the citric. The history of the Malic acid is first to be given.

The process which Scheele gave for its extraction, is to saturate the expressed juice of unripe apples by the addition of carbonate of potash: to the saturated liquid, acetate of lead is added as long as there is any precipitation: the precipitate, which is the compound of malic acid, and oxide of lead, is washed, and diluted sulphuric acid is added until the mixture has a perfectly acid taste, without any sweetness: the malic acid thus disengaged is separated by filtration from the sulphate of lead *. Mr Donovan has remarked, that the precipitation of the oxide of lead by sulphuric acid is objectionable, as it is difficult to adjust the proportions so as to do it perfectly, without leaving free sulphuric acid. And the juice of the apple, he finds, contains a portion of another acid, what he has named the Sorbic, which remains mixed with the malic.

When the malic exists in combination with citric acid, the process which Scheele employed to separate them, was to evaporate the expressed juice to the consistence of honey, and then dissolve it in alkohol: the mucilaginous matter was thus removed. This liquor being filtrated, the alkohol was evaporated, and to the remaining acid fluid twice its weight of water was added. It was then saturated with chalk: the citric acid forms with the lime of the chalk an insoluble compound, the precipitation of which is promoted by boiling the liquor a little. The compound of lime and malic acid remaining in solution is precipitated by alkohol; the malate of lime may then be decomposed by the addition of acetate of lead, and the malate of lead thus obtained decomposed by sulphuric acid, as in the preceding process. In this method the mucilage of the fruit is more completely separated by the previous addition of the alkohol, than in the other.

Malic acid can be artificially formed. Sugar, when acted on by nitric acid, is converted principally into oxalic

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* Crell's Chemical Journal, vol. ii. p. 7.

acid; but Scheele observed, that a quantity of malic acid is also produced. If the oxalic acid be separated, by adding lime-water as long as there is any precipitation, there remains in solution the malic acid, which may be separated by a process similar to that last described. The execution of this process is, however, attended with difficulty.

Vauquelin found, that the acid contained in the *Sempervivum* tectorum, is the malic acid combined with lime; and, according to Mr Donovan, the acid is extracted from this plant in greater purity than from any other vegetable*.

Malic acid is not susceptible of crystallization. By this it is distinguished from the other vegetable acids, and is also capable of being more easily detected when mixed with them, as it forms the uncrystallizable residue of the liquid from which they have crystallized. When much evaporated, it becomes thick and viscid; and is deliquescent. Its solution is of a brownish red colour, has a very sour taste, and reddens deeply the vegetable colours.

When exposed to heat, it is easily decomposed: its colour darkens; it swells, exhales an acrid vapour, and leaves a voluminous coal. When subjected to destructive distillation, the products are empyreumatic acetic acid, carbonic acid gas, with carburetted hydrogen, and charcoal. The proportions of its elements have not been determined.

Malic acid, in the state of its watery solution, soon suffers spontaneous decomposition.

It is decomposed by the more powerful acids: sulphuric acid chars it: nitric acid converts it into oxalic acid.

It unites with the alkalis and earths, forming salts denominated Malates, the properties of which have scarcely been examined but by Scheele. With the alkalis it forms salts, which are deliquescent. With lime it forms a salt, when neutral, in small irregular crystals, which require a large quantity of boiling water for their solution; but when there is a slight excess of acid, they are readily soluble in cold water. In combining with barytes, the results are similar. By the comparative solubility of these combinations with this earth, it is easily distinguished from oxalic and some of the other vegetable acids. With alumina it affords a neutral salt, which is not easily soluble in water; with magnesia, a deliquescent salt.

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* Philosophical Transactions, 1815.

Malic acid acts on some of the metals. Scheele observed, that it dissolves iron and zinc: the solution of malate of iron is brown, and not crystallizable; that of zinc yields regular crystals. He adds, that upon the other metals it has no perceptible effect. It combines, however, with their oxides, and, in consequence of such combinations, causes precipitates in several of the metallic solutions. It precipitates, in particular, the nitrates of mercury, lead, and silver. It also decomposes the solution of gold, and even reduces the oxide to the metallic state.

SECT. XXI.—OF SORBIC ACID.

THE name of SORBIC ACID has been given by Mr Donovan to an acid, which he found to be associated with the malic acid in the berries of the Sorbis aucuparia, and in several other fruits. Scheele had stated, that the acid in these berries is the malic; but Mr Donovan observed, that when the juice is precipitated by acetate of lead, the liquid that passes through the filtre deposites crystals, and malate of lead does not crystallize. It contains, therefore, another acid along with the malic, which gives this result. They are separated by adding to the juice acetate of lead; the compounds of oxide of lead, both with the malic acid and the other acid, are precipitated. The compound with the latter is, by the affusion of boiling water, resolved into a super and a sub-salt; the former is held in solution, but, as the solution cools, the neutral compound is deposited in crystals. When this action of boiling water ceases, the more powerful action of diluted sulphuric acid is employed to disengage the free acid. The whole of the crystallized product is collected, and submitted to the action of diluted sulphuric acid at a boiling heat for half an hour, supplying water to keep up the evaporation. The clear liquor is filtered, and, while still hot, sulphuretted hydrogen is transmitted through it; and when all the oxide of lead has been precipitated, it is boiled down, and left exposed to the air to discharge the excess of sulphuretted hydrogen: the pure acid is thus obtained. It is transparent, colourless, and inodorous; soluble in alkohol, and in water in every proportion. When evaporated it forms an uncrystallizable mass, which is deliquescent: its taste is intensely sour; it does not rise in distillation, and it is scarcely liable to spontaneous decomposition. With potash, soda, and ammonia, it forms salts, which, when there is an excess of acid in the combination, form permanent crystals. With lime and barytes it forms insoluble neutral salts: with magnesia a salt soluble and crystallizable: with alumina it cannot be combined. In these combinations, as well as in that with oxide of lead, it differs from malic acid. It also decomposes malate of lead.

The discovery of this acid has lately been confirmed by Braconnot and Vauquelin. The latter chemist remarks, that it may be obtained in crystalline grains, from its solution evaporated to the consistence of syrup. These are volatilized by a moderate heat without decomposition, and the acid condenses in slender needles. He states its composition, in the state in which it exists in sorbate of lead, at carbon 28.3, oxygen 54.9, and hydrogen 16.8. Braconnot has remarked, that it is extensively diffused in the vegetable kingdom. In verjuice it exists in considerable quantity *.

SECT. XXII.—OF CITRIC ACID.

IT is this acid which exists in the juice of the lemon and lime, and gives it its sourness. It is mixed with mucilaginous and extractive matter; and we are indebted to Scheele for the process by which the acid is obtained pure. It consists in saturating the expressed juice of the lemon, by the addition of chalk. The citric acid, combining with the lime, forms an insoluble compound, which precipitates. This is washed with warm water, to remove the mucilage and extractive matter. The citrate of lime is then subjected, in a matrass, to the action of as much sulphuric acid, previously diluted, as is sufficient to saturate the lime of the quantity of chalk that has been employed. The citric acid is disengaged and dissolved by the water: the mixture is boiled for a few minutes, to facilitate the precipitation of the sulphate of lime, and is filtered. The filtered liquor is evaporated to the consistence of syrup, any sulphate of lime separated during the evaporation being withdrawn; and, on cooling and standing for some time, the citric acid is obtained in needle-like crystals. Scheele found it useful to add a slight excess of sulphuric acid; and Dizé † has remarked, that this is requisite to decompose and facilitate the separation of a portion of mucilage or extractive matter, which adheres to the citric acid when it combines with the lime, and which, when the acid is afterwards disengaged, opposes its crystallization. Proust has observed, how-

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* Annales de Chimie et Physique, tom. vi.

† Nicholson's Journal, 4to, vol. ii. p. 43.

ever, that if too great an excess of sulphuric acid be used, it re-acts on the citric acid itself, and chars it, and the evaporated fluid does not crystallize *. He has added some facts, with regard to the proportions, that may be useful in conducting the process. Four ounces of chalk, saturated with lemon juice, required for the saturation 94 ounces; and from this 7½ ounces of dry citrate of lime were obtained. The four ounces of chalk required for its saturation 20 ounces of a diluted sulphuric acid, composed of one part of the common sulphuric acid, with three of water; and, of course, this is the quantity of that acid to be used in decomposing this quantity of citrate of lime.

Citric acid exists in a number of other fruits, from which it may be extracted, and what is at present found in the shops, is often prepared from the juice of the lime. From Vauquelin's analysis of the pulp of the tamarind †, it appears to be the chief acid constituent of that fruit.

Citric acid obtained by a first crystallization, is not perfectly white, but it becomes so when the crystallization is repeated. Its crystals, when regular, are rhomboidal prisms, acuminated by four planes: they contain, according to Berzelius, 17 of water of crystallization. Its acid powers are considerable: its taste is extremely sour, and almost caustic; and it instantly reddens the vegetable colours.

Exposed to heat, the crystals melt, from the solvent power of their water of crystallization; by the continuance of the heat, the acid suffers decomposition, exhales an acrid vapour, and is reduced to a coal. Subjected to destructive distillation, it affords an acid liquor, which appears to be the acetic, and afterwards carbonic acid gas and carburetted hydrogen, leaving a light charcoal. Decomposed by the action of hyper-oxymuriate of potash at a high tem-

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* Philosophical Magazine, vol. x. p. 112.

† Annales de Chimie, tom. v. p. 104.

perature, the products, according to Gay Lussac's analysis, give as the proportions of its elements, carbon 33.811, oxygen 59.859, hydrogen 6.330. Berzelius states the composition from the products of the combustion of the acid combined with oxide of lead, at carbon 41.369, oxygen 54.831, hydrogen 3.800. But in this combination a portion of water has been abstracted from it, which he regarded as the combined water of the acid, but which is to be considered as water formed from the combinations of portions of the oxygen and hydrogen of the acid. Estimating the quantity of water, on the principle already assigned, from the quantity of base which the acid saturates, it amounts on 100 of the real acid of Berzelius to 13.59 of oxygen, and 1.1 of hydrogen; and adding these to the above proportions, the composition is carbon 41.37, oxygen 68.42, and hydrogen 4.9, which, with some deficiency in the proportion of the last element, agrees nearly with the composition assigned by Gay Lussac. The proportion of oxygen to carbon is that which may be considered as intermediate between carbonic oxide and carbonic acid. The hydrogen is nearly in what may be regarded as the first proportion of that element to carbon, the same as in gallic acid.

This acid is very soluble in water. At a moderate temperature, 100 parts of water dissolve, according to Vauquelin, 75 parts, cold being produced during the solution; at 212°, it dissolves twice its weight of it. Like the other vegetable acids, its solution undergoes spontaneous decomposition, though not very readily.

The more powerful acids decompose it, though with difficulty. Concentrated sulphuric acid converts it, according to Fourcroy, into acetic acid. Scheele remarked, that nitric acid did not convert it, as it does some of the other vegetable acids, into oxalic acid; but Fourcroy and Vauquelin found, that when acted on by a large quantity of nitric acid, it affords a small portion of oxalic, with acetic acid.

Citric acid combines with the alkalis and earths, forming salts denominated Citrates; the properties of which have been examined with care by Vauquelin, the results of whose experiments have been stated by Fourcroy *.

The citrate of potash is very soluble, does not crystallize but with difficulty, and is deliquescent: its taste is saline, and rather mild. It contains 55.55 of acid, and 44.45 of alkali. Citrate of soda is likewise very soluble, requiring little more than its weight of water for its solution; it crystallizes in six-sided prisms, and the crystals are slightly efflorescent. Their taste is faintly saline: the proportions of the solid salt are 60.7 of acid, and 39.3 of soda. Citrate of ammonia is even more soluble than the others, and does not crystallize but when its solution is much concentrated: the form of its crystals is an elongated prism. It consists of 62 of acid, and 38 of ammonia. The earthy citrates are in general less soluble. When the solution of barytes is poured into the acid, a precipitate, soluble in the liquid by agitation, is formed; when the whole is saturated, the salt is deposited in a kind of crystalline powder, which a large quantity of water dissolves. It consists of 50 of acid, and 50 of base. When citric acid is saturated by lime, small crystals are deposited, which are very sparingly soluble: 100 parts contain 62.66 of acid, and 37.34 of lime. When saturated by magnesia, the concentrated solution does not crystallize regularly, but assumes the state of a white, opaque, and spongy salt. Its proportions are 66.66 of acid, and 33.34 of base.

Vauquelin has likewise examined the action of citric acid on the metals. It does not dissolve silver, but it combines with its oxide, and forms a salt insoluble, of a harsh metallic taste, and which, like the other salts of silver, is blackened by light: it is also decomposed by heat, leaving metallic silver intermixed with charcoal. It consists of 36

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* System of Chemical Knowledge, vol. vii. p. 282.

of acid, and 64 of oxide. Quicksilver is scarcely more acted on by citric acid, but its oxide combines with it: the red oxide, when added to the acid, causes an effervescence, and becomes white and solid: the salt is not perceptibly soluble in water, but is decomposed by it, the water becoming milky. It is decomposed by heat, and the oxide is reduced. Zinc is dissolved by a solution of citric acid, hydrogen gas being disengaged; and the solution yields small brilliant crystals insoluble in water: 100 parts of this salt contain nearly equal parts of acid and oxide. Iron is dissolved in the same manner: the solution is of a brown colour, and by spontaneous evaporation deposites small crystals. This salt is very soluble in water; its taste is very astringent: it consists of 30.38 of oxide, and 69.62 of acid. Citrate of lead, which is insoluble, consists of 34.18 of citric acid, and 65.82 of oxide of lead.

As affording chemical characters by which this acid may be distinguished, it may be added, that solutions of the acetates of magnesia, lime, and alumina; of the muriates of barytes, lime, alumina, and magnesia; and of the nitrates and sulphates of these substances, undergo no apparent change from the addition of citric acid. The muriates and nitrates of zinc, the sulphate, muriate, nitrate, and acetite of copper, are not decomposed by it; acetate of lead gives a precipitate of a white powder: nitrate and acetate of mercury are also decomposed, and a precipitate of a brick-red colour thrown down: acetate and sulphate of iron in solution, receive from it a green tinge[*]. All the alkaline citrates are precipitated by the solution of barytes: the precipitate which they form with calcareous salts, is soluble in less than 500 parts of water. The oxalic and tartaric acids decompose them, and form crystallized or insoluble precipitates[†].

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[*] Dizé, Nicholson's Journal, 4to, vol. ii. p. 45.

[†] Vauquelin, Fourcroy's Chemistry, vol. vii. p. 286.

Citric acid, in its crystallized state, can be preserved for any length of time without decomposition; and a grateful lemonade may be prepared from it, by dissolving 30 or 40 grains in a pint of water, with the addition of a little sugar, and to communicate flavour, of a little lemon peel, or of a powder formed by rubbing sugar on the fresh lemon. The lemon juice may be regarded as a specific in scurvy; it is uncertain whether or not the crystallized citric acid may be equally effectual.

SECT. XXIII.—OF OXALIC ACID.

It has been long known, that a crystallized acid salt may be procured from the juice of some of the species of sorrel, particularly the Oxalis acetosella. Margraaf observed the existence of potash in this salt; but the nature of its acid was not well determined. Bergman made public the fact, which is said to have been discovered by Scheele, that sugar, when subjected to the action of nitric acid, affords an acid of a particular nature, the properties of which he also stated; and some time afterwards Scheele discovered, that the acid which exists in the salt of sorrel is of the same nature; that it may be extracted from that salt, and obtained pure; and that a salt analogous to the salt of sorrel may be formed, by combining the acid prepared from sugar, with such a quantity of potash as shall leave an excess of acid. To this acid, thus existing as a vegetable product, and capable also of being artificially formed, the name of Oxalic has been given.

The native salt of sorrel, the super-oxalate of potash, is extracted from the juice of the sorrel, by the following process: The leaves of the plant are bruised with a little water, and the juice expressed; the impurities are allowed to subside, and the separation of any foreign matter is facilitated by heating it slightly: it is clarified by adding to it water, in which a small portion of fine clay has been suspended, and with which it is agitated. The clarified juice is put into boilers of tinned copper, and is boiled gently, until a pellicle forms on its surface: it is put aside for a month, in earthen vessels: a salt crystallizes on the sides of the vessel, of a greyish colour; and fresh quantities of this are obtained, by renewing the evaporation and clarification. The whole salt is purified by a second crystallization, and is obtained white in four-sided prisms [*]. It is known in the shops under the name of Salt of Lemons, and is used principally for removing stains from ink.

Scheele obtained the acid from this salt, by adding to its solution in water a solution of acetate of lead, as long as there is any precipitation. The precipitate is the oxalate of lead. It is washed with water, and decomposed by the addition of sulphuric acid; the proportion of this being estimated from the quantity of it, known by a previous experiment to be necessary for the decomposition of the quantity of acetate of lead employed. The oxalic acid is obtained by slow evaporation, in regular prismatic crystals [†].

The same acid exists in other species of sorrel, and in some other vegetables. The earthy-like matter disseminated in streaks in the root of rhubarb, Scheele found to consist of oxalic acid, combined with lime [‡]; he found it also in the roots of bistort, liquorice, squil, turmeric, tormentil, ginger, &c. and in the barks of cannella, cascarilla, cinnamon, quassia, oak, elm, and others [||]. Deyeux found, that the acid juice contained in the fibres of chick pease is oxalic acid; though Dispan has since stated some imperfect experiments, from which he considered the acid from this vegetable to be a peculiar one, to which he gave the name of Ciceric *.

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[*] Annales de Chimie, tom. xiv. p. 7.

[†] Crell's Chemical Journal, vol. i. p. 108.

[‡] Ibid. vol. i. p. 54.

[||] Ibid. vol. iii. p. 1.

The artificial formation of this acid from sugar is effected according to the process described by Bergman. One ounce of refined sugar, in powder, is mixed in a tubulated retort, with three ounces of nitrous acid: when the solution is completed, and the disengagement of gas has ceased, the solution is to be gently boiled. When it acquires a dark brown colour, three ounces more of nitrous acid are to be added, and the boiling continued until the coloured and smoking acid has entirely disappeared. The liquor in the retort being poured out, it deposites on cooling slender crystals, being quadrangular prisms; when dried on bibulous paper, they weigh 109 grains. The remaining liquor, boiled with two ounces of nitrous acid until the red vapours begin to disappear, on cooling affords 43 grains of crystals †. The quantity, however, is liable to vary; for if the nitric acid be boiled too long, a portion is decomposed, and the crystallized product is diminished. The crystals require to be rendered pure by repeated solutions and crystallization.

The changes effected in this production of oxalic acid from sugar, are not precisely ascertained. Oxygen is communicated from the nitric acid; but it is uncertain how this operates in the production of the acid. From the small quantity of acid obtained from a given quantity of sugar, it is obvious that it does not merely combine with the saccharine matter to acidify it, but probably unites with portions of its carbon and hydrogen, forming water and carbonic acid, and leaving the remaining elements in those proportions which constitute oxalic acid. There is

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* Annales de Chimie, tom. xxx. p. 179.

† Bergman's Essays, vol. i. p. 304.

also a formation of malic acid, which remains in the uncrystallizable liquor.

This acid is formed from other vegetable substances subjected to a similar process. Bergman obtained from 100 parts of gum-arabic about 26 of acid; from 8 of alkohol, 3 parts; and from a number of vegetable products a greater or less quantity. It is even afforded by some animal substances, when they are acted on by nitric acid so as to disengage their nitrogen.

Oxalic acid crystallizes in slender four-sided rhomboidal prisms, bevelled at each extremity. The crystals are of a white colour, transparent, permanent in the air, or slightly efflorescent. They contain water of crystallization: so that when heated on a sand bath they fall into powder, and lose weight: but as the acid is partly volatilized, the quantity cannot be estimated from this: from the water which appears to be separated from it in its combination with lime, Dr Thomson estimates it at 23 per cent. By neutralizing a given weight of the crystallized acid with ammonia, and precipitating by muriate of lime, Berard obtained a result, whence he inferred that it contains 27.3 per cent. The taste of the crystals is very sour, and they communicate this, as well as the power of reddening the vegetable colours, to a large quantity of water. Twenty grains give a sensible acidity to three pints. They are soluble in twice their weight of cold water, and in an equal weight of boiling water. They are also soluble in alkohol; 100 parts when boiling, taking up nearly 56 of the acid, but at an inferior heat not above 40. They dissolve in sulphuric ether, though with difficulty *.

Exposed to heat, the acid suffers aqueous fusion: when it begins to boil, it becomes brown, and is decomposed; an acid liquor passes over; an acid powder is condensed in the neck of the receiver, which is the oxalic acid, extreme-

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* Bergman's Chemical Essays, vol. i. p. 508. &c.

ly pure, the residuum being a brown or grey matter; and a large quantity of elastic fluid is disengaged during this decomposition, of which about one-half is carbonic acid; the other is inflammable. When the sublimed portion of acid is again subjected to the same operation, it is partly sublimed, and partly resolved into an acid liquor not crystallizable; and by repeating this a third time, the decomposition is completed.

The composition of this acid has been very variously estimated. From its not yielding empyreumatic oil in its decomposition, it seemed to contain little hydrogen; the large quantity of carbonic acid it affords, indicated the presence of a large proportion of carbon; and from the other vegetable acids being converted into it by oxygenation, it was inferred to contain a large proportion of oxygen. But the proportions have been variously assigned. Part of the discordance has arisen from the presence of water of crystallization, and the difficulty of abstracting this entirely. To obviate this it has been submitted to analysis in the state of oxalate of lime. This salt decomposed by heat, yields carbonic acid, carbonic oxide, carburetted hydrogen, water, and charcoal: from the quantities of these Dr Thomson inferred, that oxalic acid consists of carbon 31.78, oxygen 64.69, and hydrogen 3.53 *. Gay Lussac and Thenard decomposed dry oxalate of lime, by the action of oxymuriate of potash, and assigned as the proportions, carbon 26.566, oxygen 70.689, hydrogen 2.745. But the acid in this combination contains, according to the notion which has been of late years adopted by chemists, combined water, the quantity of which, according to the experiments of Vogel, is about 20 per cent. To remove this, and determine the composition of what is considered as the real acid, Berzelius operated on it, in conformity to his usual method, in the state of oxalate of lead. He

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* Philosophical Transactions, 1807.

found the composition, carbon 33.222, oxygen 66.534, hydrogen 0.244. And if the results of Gay Lussac's analysis be corrected by abstracting the water of composition, they are very nearly the same *.

In conformity to the theory of the constitution of the vegetable acids which I have illustrated, oxalic acid is to be regarded as having carbon for its radical, acidified by oxygen and hydrogen. The water of crystallization is to be abstracted from it in estimating its composition; but the water of combination abstracted in the process of Berzelius, is water formed by the combination of portions of the oxygen and hydrogen of the acid. If these be added to the composition he states, they give as the proportions, carbon 26.5, oxygen 71, and hydrogen 2.5, coinciding almost exactly with those assigned by Gay Lussac.

This proportion of oxygen to carbon is evidently precisely that constituting carbonic acid, 100 of this acid being composed of 27.4 of carbon, and 72.6 of oxygen;—oxalic acid therefore differs from carbonic acid merely in the addition of a proportion of hydrogen; the one is the binary, the other the ternary compound. The hydrogen is to the carbon in the first or lowest proportion in which it appears to combine with that element; that is, half the quantity in which it exists in super-carburetted hydrogen †.

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* Annals of Philosophy, vol. v. p. 99.

† The analysis of oxalic acid, as given by Berzelius, presented a difficulty in the atomic theory, in the proportion of hydrogen. The quantity is so small, compared with the other elements, as to amount only to a fraction of an atom, which is an absurdity. It was therefore endeavoured to be shewn, that the proportion of hydrogen which he assigned was under-rated, but without success. It is in fact over-rated; or rather, when the supposed water of composition is abstracted, there is no hydrogen in what is called real oxalic acid, and the small quantity supposed to exist is to be referred to error of analysis. The difficulty, it is obvious, is removed in the view which I have given of the constitution of the acid.

The relation of oxalic acid to carbonic acid is, according to this view, analogous to that of muriatic to oxymuriatic acid,—the proportion of oxygen to the radical being the same, the presence of hydrogen constituting the only distinction, and this hydrogen being expended in the formation of water, from the action of a salifiable base. The proportion of oxygen and carbon in a dry oxalate, are thus evidently those which constitute carbonic acid, for although in the action of the acid on the base, a portion of its oxygen is abstracted in forming water, an equivalent quantity is added from the oxide constituting the base; and, analogous to the general view I have stated, a ternary compound is established.

Oxalic acid combines with the alkalis and earths, forming salts named Oxalates, of which those with alkaline bases are soluble and crystallizable; those with the earths are in general of sparing solubility. With those bases with which it forms soluble compounds, it has a strong tendency to establish combinations with an excess of acid; and these super-oxalates are less soluble in water than the oxalates,—circumstances, as Berard has remarked, which may be ascribed to the influence of the force of cohesion in the acid, augmented by combination with the base. These salts, too, exemplify, in a striking manner, as was shewn by Dr Thomson, by Dr Wollaston *, and by Berard †, the general law with regard to definite proportions in saline compounds, that in the two combinations the quantity of acid in the super-oxalate is double the quantity of what is contained in the oxalate. These chemists have determined the composition of the oxalates and super-oxalates, though with some discordant results; and more lately the analysis of several of them has been given by Vogel ‡. In the

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* Philosophical Transactions, 1807, 1808.

† Annales de Chimie, tom. lxxiii. Nicholson's Journal, vol. xxxi.

‡ Annals of Philosophy, vol. v. p. 29.

analysis of the latter, the estimates refer to the acid more completely free from water than in the former: hence the proportion of it is stated lower.

Oxalate of potash, when neutral, is so soluble that it is not easily crystallized; its solution on evaporation becoming gelatinous; but, if there be a slight excess, either of acid or alkali, crystals are formed. Dr Thomson found, however, that it crystallizes easily in flat rhomboidal prisms: its taste is cool and bitter; at 60° it dissolves in thrice its weight of water. It consists, excluding the water of crystallization expelled by a heat of 212°, of 44.87 of acid, and 55.13 of base, and in this state appears to retain nearly 10 per cent. of water. According to Berard, its composition dry, is potash 50.68, oxalic acid 49.32, and crystallized, potash 42.12, acid 40.57, water 17.31. According to Vogel, it consists dry, of potash 57, acid 43.

The super-oxalate of potash is easily formed; crystals are deposited, on adding oxalic acid to a solution of the oxalate, or merely by dropping a solution of potash into a solution of oxalic acid; when formed by evaporation, they are four-sided prisms: it also exists, as has been already remarked, as a native production in the juice of the leaves of the sorrel, and in other plants; its taste is sour, and it reddens the vegetable colours; it is sparingly soluble in cold water; at 212° six parts of water dissolve it. Its solution does not decompose spontaneously, as those of almost all the salts containing acids of vegetable origin do. The stronger acids decompose it partially with difficulty: the alkaline, and some of the earthy bases, as barytes and magnesia, enter into combination with its principles, and form triple salts. Lime decomposes it by attracting its acid. This salt contains just double the quantity of acid that the neutral oxalate contains. According to Berard, it consists dry, of potash 34.2, oxalic acid 65.8. 100 of potash, therefore, combine in the one salt, according to his analysis, with 97.3 of acid, and in the other with 192.4 of acid. According to Vogel, the crystallized super-oxalate, or bin-oxalate, consists of 31.44 of potash, 55.93 of acid, and 12.63 of water; the dry salt of 35.98 of potash, and 64.02 of acid.

A quadroxalate of potash, that is, a salt containing four times the quantity of acid of what the neutral oxalate contains, exists. Dr Wollaston pointed it out *. He obtained it in decomposing the super-oxalate by nitric or muriatic acid; half the quantity only of potash was abstracted by either of these acids, and a salt crystallized after solution, which of course contained four times as much acid as would saturate the remaining potash: the same salt is obtained by boiling oxalic acid in a solution of muriate of potash. Its being less soluble than either the oxalate or super-oxalate, appears to be the circumstance, as Berard has remarked, that determines its formation. It is singular that the intermediate combination between the double and quadruple proportion of acid cannot be formed, as Dr Wollaston found by experiment, which is probably owing to this circumstance of the force of cohesion determining rather the formation of the super-oxalate and quadroxalate; though Dr Wollaston gives an hypothesis to account for it on the atomic doctrine. According to that doctrine, this combination ought to take place as readily as the others; for if, as must be supposed, the neutral oxalate consists of 1 atom of base with 1 of acid, and the others of 1 of base with 2 of acid and 4 of acid, that of 1 with 3 ought equally to exist. The composition of the quadroxalate, as determined by Berard, is potash 18.95, oxalic acid 72.05, water 9. Hence 100 of potash are combined with 381 of acid.

Oxalate of soda is not very soluble, and can scarcely be obtained in regular crystals, being precipitated when formed, in crystalline grains. Dr Thomson states, however,

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* Philosophical Transactions, 1807.

that it crystallizes readily; when heated, it loses its water of crystallization, and in this dry state consists of 63.63 of soda, and 36.37 of acid: according to Berard, of 58.92 of soda, and 41.08 of acid: according to Vogel, of 45.23 of soda, and 54.77 of acid. This base is also disposed to combine and crystallize with an excess of acid, forming a salt less soluble than the neutral oxalate, and composed, according to Berard, of 25.57 of soda, 72.80 of acid, and 1.63 water. It contains, therefore, twice the quantity of acid in the other, 100 of soda being combined in the first with 143.5, and in the second with 284.7 of acid.

The compound of oxalic acid with ammonia, is obtained by slow evaporation in quadrangular rhomboidal prisms: of which, at the temperature of 60°, 1000 grains of water dissolve only 45 grains. When dried at 212°, it consists, according to Thomson, of 74.45 of acid, and 25.53 of base: according to Berard, it consists of 72.34 of acid, and 27.66 of base. A super-oxalate of ammonia likewise exists, less soluble than the oxalate, which, according to the same chemist, consists of 73.4 of acid, 14 of ammonia, and 12.6 of water. In these salts, therefore, the same ratio of acid of 1 and 2 exists, 100 of base in the one being combined with 261.4, in the other with 523 of acid.

Oxalate of barytes is formed in small crystalline grains, when oxalic acid is saturated by the addition of barytic water, or when a soluble oxalate is added to the solution of a barytic salt. It is sparingly soluble in water, and is insipid. When dry it consists, according to Dr Thomson, of 58.84 of barytes, and 41.16 of acid; according to Berard, of 62.17 of barytes, and 37.83 of acid. A super-oxalate is also formed, by boiling crystals of oxalic acid in a solution of muriate of barytes; on cooling, the super-oxalate is deposited in crystals; the excess of acid is detained however by so weak an affinity, that merely boiling in water abstracts it. The super-oxalate consists, according to Berard, of 45 of barytes, and 55 of acid. It contains therefore twice the quantity of acid that the other does, 100 of barytes in the oxalate being combined with 60.84, and in the other with 123 of acid.

Oxalate of strontites is less soluble than oxalate of barytes, and is indeed nearly insoluble. Dr Thomson had stated its composition at 60.23 of strontites, and 39.77 of acid. But, as Berard has remarked, this would infer that barytes has a greater capacity for saturation than strontites, which, with regard to all the other salts of these earths, is not the case. He states the composition at 54.46 of strontites, and 45.54 of acid. Dr Thomson had concluded, that another compound, containing 43.1 of strontites, with 56.9 of acid, is formed by decomposing muriate of strontites by oxalate of ammonia; but Berard has shewn, that this compound, which would be a super-oxalate, does not exist.

Oxalic acid abstracts lime from all its saline compounds, forming a compound nearly or altogether insoluble, which is precipitated; hence the formation of this compound, on the one hand, forms the most delicate test of the presence of oxalic acid, and on the other, of the presence of lime. In the latter respect it is of much importance that the composition of this oxalate should be determined, as from it most frequently are estimated the proportions of lime in chemical analysis; at the same time a difficulty attends this, from the uncertainty of its being entirely free from water. The proportions assigned, however, by Thomson and Berard, very nearly agree. When thoroughly dried by exposure for a considerable time to the heat of a steam or sand bath, it consists, according to the former, of 37.5 of lime, and 62.5 of acid; according to the latter, of 38 of lime, and 62 of acid. When merely dried in the open air, it retains a portion of water; this amounts, when it is dried slowly at 60, according to Dr Thomson, to 5.3 per cent., or when dried hastily, even to 10 per cent. Other results have also been stated with regard to the composition of this salt. Vogel states the proportions at 38.5 of lime, 49.5 of acid, and 12 of water, and when dry 43.75 of lime, and 56.25 of acid. These agree almost exactly with Dr Wollaston's scale of chemical equivalents. At the same time, as the oxalate cannot bear exposure to a red heat, there must always be some uncertainty with regard to the water which may be contained in it; and the quantity of lime, when it is employed as a medium of analysis, is best determined by its decomposition by heat. No super-oxalate of lime exists, nor does the neutral oxalate appear to be sensibly dissolved by an excess of oxalic acid. It is dissolved, however, very sensibly by other acids, as the nitric and muriatic, even in a slight excess,—a circumstance sometimes requiring to be attended to in analysis, to obviate error from the action of any acid evolved.

Oxalate of magnesia, formed by saturating oxalic acid by magnesia, is a soft white powder; tasteless, and not sensibly soluble in water; yet, on adding oxalate of ammonia to a solution of a magnesian salt, no precipitate, or only a very sparing one, is thrown down. If the liquor be concentrated, however, it is slowly deposited; or if heated, immediately, or if it be evaporated to dryness, and re-dissolved, the oxalate of magnesia remains. It consists, according to Dr Thomson, of magnesia 26.32, acid 73.68; according to Berard, of magnesia 27.35, acid 72.65.

Oxalate of alumina is formed by digesting the earth in oxalic acid: the solution on evaporation yields a yellowish pellucid mass, of a sweetish astringent taste, which, when dry, deliquesces in a moist atmosphere: it is sparingly soluble in alkohol. Bergman states the proportions of its constituent parts at 44 of earth, and 56 of acid and water.

Oxalic acid acts on several of the metals, especially those which are able to decompose water so as to become oxidated; it unites with their oxides; and it decomposes a number of the metallic salts: with some of them super-oxalate of potash combines, so as to form ternary compounds. The principal metallic oxalates have been described by Bergman, and a few facts with regard to them have been added by Fourcroy.

On oxide of gold the acid scarcely exerts any action but blackening it. It dissolves precipitated oxide of platina, and forms a yellow liquid, which affords crystals of the same colour. It precipitates oxide of silver from its solution in nitric acid, forming a white powder scarcely soluble in water, and still less so in alkohol; soluble in nitric acid, and blackened by the action of the solar rays; and which, heated in a spoon over burning fuel, is dispersed with a kind of fulmination. Oxide of mercury is dissolved, forming a white pulverulent salt, not soluble in water, unless it has an excess of acid, and which is blackened from exposure to the sun: it also fulminates when heated. Copper, in the metallic state, is acted on by this acid; and with still more facility when it has been oxidated: a powder is formed of a pale blue colour, scarcely soluble in water. Iron is dissolved by it with a disengagement of hydrogen gas: the solution has an astringent sweetness, and, when prepared without heat, exhibits prismatic crystals of a greenish-yellow colour, soluble in water, which retain an excess of acid. The solutions of iron highly oxygenized, are precipitated by the acid in a powder of a fine red colour. Lead digested with oxalic acid is corroded, but scarcely dissolved; but when in the state of an oxide combines with it, and the solution, when approaching to saturation, forms crystalline grains, which subside, and are scarcely soluble in water, except from an excess of acid: the oxalate of lead is also precipitated in a powder, when an oxalate is added to the solution of a salt of lead; it consists, according to Berzelius, of oxalic acid 24.54, of lead 75.46. Oxalate of tin is formed by the action of the acid on the metal assisted by heat: the solution has a styptic taste, and exhibits prismatic crystals, or when evaporated quickly to dryness, a horn-like mass.

Zinc is dissolved with strong effervescence, from the disengagement of hydrogen gas; a white powder is formed, not soluble in water, unless from an excess of acid. With oxide of bismuth a white pulverulent salt is formed, scarcely soluble in water; and a similar compound in transparent grains is slowly deposited on the addition of oxalic acid to nitrate of bismuth. Nickel digested with the acid is covered with a greenish-white crust; and a powder of a similar appearance is precipitated by it from the salts of nickel, soluble in water in small quantity. Cobalt is converted by it into a powder of a pale rose colour, scarcely soluble in water, but becoming soluble from an excess of acid; and a similar compound is formed by the addition of the acid to any of the salts of cobalt. Black oxide of manganese effervesces with oxalic acid, probably from the disengagement of oxygen gas; and the saturated solution deposites a white powder scarcely soluble in water, unless the acid be in excess: this is also formed by the addition of the acid to the solutions of manganese. Antimony in the state of oxide is dissolved slowly: the solution in which the acid is predominant, affords crystalline grains, which are scarcely soluble in water. White oxide of arsenic is easily dissolved; and the solution on evaporation affords prismatic crystals, which, melting with a gentle heat, emit the superabundant acid: they are sublimed and decomposed by heat.

Oxalic acid is chiefly employed as a test to discover lime. Its delicacy is very great. According to Bergman, one grain of the concrete acid of the size of a pin's head, discovers one grain of pure lime in 42.250 grains of water, by the cloud it produces. It is rendered less delicate by the presence of any free acid, either existing in the liquid, or disengaged from combination with the lime, the acid retaining a little of the oxalate dissolved; hence any free acid ought to be neutralized by ammonia, and oxalate of ammonia, instead of pure oxalic acid, should be used.

Brugnatelli published some experiments, to prove that oxalic acid is a less delicate test of lime than had been supposed [*]; but Darracq shewed that the conclusion is incorrect [†].

Super-oxalate of potash, the native salt of sorrel, is used under the name of Salt of Lemons, to remove ink-stains from linen; an effect it produces by the oxalic acid dissolving the oxide of iron in the ink, on the combination of which with the tannin and gallic acid the colour depends; while, at the same time, it can be used without any risk of injury to the cloth.

Oxalic acid appears to be poisonous in its action on the animal system: 4 drachms of it swallowed by an individual by mistake occasioned death, and afterwards it was found that much smaller quantities killed animals. Hence the danger of the substitution of it, which is sometimes practised, for citric acid. Chalk swallowed diffused in water forms the best antidote [‡].

SECT. XXIV.—OF TARTARIC ACID.

A SALINE matter is deposited slowly from wine, which has been long known by the name of Tartar, and, when purified from the colouring matter which adheres to it, by that of Crystals or Cream of Tartar. It was known to the older chemists, that potash could be obtained from it by calcining with a moderate heat; and it was by this process that this alkali was generally obtained for chemical and medicinal use. Lefevre, Glazer, and others, maintained that this alkali pre-existed in the salt; and this was more clearly established by Duhamel, Margraaf, and Rouelle. The acid which exists in it is in excess, so to be obvious by the sour taste and acid powers of the salt. Scheele gave the process by which it could be extracted, and thus discovered the properties of this acid in its pure state. It was named Tartarous Acid, and now, to give uniformity of termination, Tartaric Acid.

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[*] Annales de Chimie, tom. xxix. p. 174.

[†] Ibid. tom. xlv. p. 68.

[‡] Philosophical Magazine, vol. xlvi. p. 70.

Tartar, or super-tartrate of potash, as it is properly named, is proved, by the experiments of Boerhaave, Neuman, and other chemists, to exist in the juice of the grape previous to its conversion into wine. It has also been discovered in other fruits, particularly in the tamarind; and it is said to exist in the roots of sage, germander, and some other plants. It exists in these, however, in small quantity, and it is the deposite from wine that is met with in commerce. It is named Red or White Tartar, according as it is more or less coloured, from the colouring matter of the wine adhering to it. Besides this, it is rendered impure by the presence of other substances, particularly tartrate of lime. It is purified by dissolving it in water, and boiling its solution with a small quantity of fine clay. This attracts the colouring and extractive matter, and the solution, on cooling, affords crystals of a white colour. These form the purified tartar, or crystals of tartar of commerce, in which, with the super-tartrate of potash, there still exists a small portion of tartrate of lime.

The process which Scheele employed to extract the acid, consisted in dissolving purified super-tartrate in boiling water, and throwing into it chalk in powder, as long as any effervescence is excited, and until the acid is saturated. The lime of the chalk combines with the excess of tartaric acid in the super-tartrate; and this tartrate of lime is precipitated, while neutral tartrate of potash remains in solution. The tartrate of lime, washed with water, is put into a glass matrass; a quantity of sulphuric acid equal to that of the chalk, and previously diluted with half its weight of water, is added. This is digested in a sand-bath for twelve hours, stirring the mixture occasionally. The sulphuric acid combines with the lime; the sulphate of lime is nearly insoluble: the tartaric acid is dissolved by the water. To ascertain that no sulphuric acid is present, a few drops of acetate of lead are added, which form a precipitate, soluble in vinegar if the tartaric acid be pure, insoluble if it be contaminated with sulphuric acid. If the latter be the case, it is digested with a little tartrate of lime, by which the sulphuric acid is abstracted. The solution is then evaporated, and the tartaric acid is obtained in a crystallized form, equal in quantity to about one-third of the super-tartrate that has been employed. Muller has given the proportions to be employed with more precision. They are 6 lbs. of chalk diffused in 36 lbs. of boiling water, and as much super-tartrate of potash as this quantity of chalk saturates: there are then to be added to the tartrate of lime, diffused in a large quantity of water, 6 lbs. of sulphuric acid, of the specific gravity of 1.817, with which 6 drachms of nitric acid have been mixed *. The sulphuric acid does not appear, in Scheele's process, to be sufficiently diluted. Lowitz has remarked, that it ought to be diluted with at least four times its weight of water †. It has been proposed to use lime instead of chalk in the process, by which the decomposition is rendered more complete, and the whole of the tartaric acid abstracted; but in this case, as Vauquelin has remarked, part of the tartrate of lime is prevented from precipitating by the action of the alkali; and it is therefore doubtful if this method is preferable to the process of Scheele.

The form of the crystals of this acid has been variously described. It occurs in thin broad tables; but it is also

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[*] Annales de Chimie, tom. vi. p. 58.

[†] Ibid. tom. xxxiv. p. 180.

obtained in prisms and in pyramids. When pure, the crystals are nearly transparent. Their taste is sour, and a small portion reddens the vegetable colours.

This acid is very soluble in water, so that a concentrated solution can be obtained of nearly an oily consistence. It is not very liable to spontaneous decomposition, especially if the solution is not very largely diluted.

Exposed to heat a little above that of boiling water, it melts without decomposition: at a higher heat it is decomposed: and by destructive distillation a considerable quantity of an acid liquor is obtained, which has received the name of Pyro-tartarous. With this, a quantity of oil is condensed in the receiver; much carbonic acid and carburetted hydrogen gas is disengaged, and a bulky coal remains. From these products Fourcroy and Vauquelin inferred that it consists of 70.5 of oxygen, 19 of carbon, and 10.5 of hydrogen, an estimate that cannot be considered as certain. The proportions assigned by Gay Lussac and Thenard, from their more accurate mode of analysis, are carbon 24.050, oxygen 69.321, hydrogen 6.629. Berzelius has stated them at carbon 35.98, oxygen 60.213, and hydrogen 3.807. But the same observations apply to these comparative results, as to those with regard to the other vegetable acids. Gay Lussac and Thenard operated on the acid in the state of tartrate of lime, in which compound it exists free from water of crystallization, or any loose adhering moisture; but without any abstraction of what is called water of combination. Berzelius, considering it necessary to abstract this supposed water, and to determine the composition of what is called the real acid, operated on it in the state of oxalate of lead, in which this condition is attained. In his analysis, therefore, there is the abstraction of those portions of the oxygen and hydrogen of the acid which form this water, and when these are taken into the calculation, the proportions are almost precisely those assigned by Gay Lussac. In these proportions the oxygen is to the carbon very nearly in that relative quantity which constitutes carbonic acid; and the deviation is not greater than what may fairly be referred to errors of analysis. The hydrogen is to the carbon precisely in that proportion which I have considered as the third of that element, that which is intermediate between carburetted and super-carburetted hydrogen. In oxalic acid it is in the first proportion; the sole difference, therefore, between these two acids is in the proportion of hydrogen.

This acid combines with the alkalis and earths, forming salts, formerly denominated Tartrites, now named Tartrates. It has a peculiar tendency to form triple salts, particularly in its combination with potash, which crystallize with regularity, and some of which are important from the uses to which they are applied.

The neutral tartrate of potash is formed by saturating the excess of acid in the super-tartrate, by the addition of the requisite proportion of alkali; a quantity of carbonate of potash being dissolved in boiling water, and super-tartrate of potash in fine powder being added in small quantities at a time, diffusing it through the solution by constant stirring, as long as there is any effervescence, and until neutralization is attained. The solution, as it is not easily crystallized, is evaporated to dryness, when this salt is prepared for medicinal use. Being more soluble than the super-tartrate, it was formerly named Soluble Tartar. Though difficult of crystallization, yet when its saturated solution is allowed to stand for some months, regular crystals form, which are tetraedral prisms, bevelled at each extremity. Its taste is bitter; it is deliquescent in a humid atmosphere, and is very soluble in water, requiring less than three times its weight of cold water for its solution. When in solution, its acid suffers a slow decomposition, so that at length its alkali remains in the state of a carbonate. A similar decomposition is effected by heat. It is very susceptible of decomposition, from the action of other acids, which abstract from it so much of its base as to reduce it to the state of super-tartrate. It consists, according to Berzelius, of 41.3 of base, and 58.7 of acid.

The Super-tartrate of potash is a salt of determinate composition, and with properties well marked. Its origin, and the method of purifying it, have been already stated. It occurs in small crystalline masses, of a white colour, and semi-transparent; brittle, and easily reduced to powder, and having a sour taste. It requires a considerable quantity of water for its solution ; about sixty parts of cold, or thirty of boiling water. Its sparing solubility affords the best test to discover tartaric acid ; a solution of potash, when added, so as to leave an excess of acid, forming a turbid fluid, from which crystals of the super-tartrate slowly subside. It is also a test to distinguish potash from soda.

When super-tartrate of potash is exposed to a strong heat, it is fused, becomes of a black colour, and is decomposed : it gives a large quantity of empyreumatic acid, an oil, with carbonic acid, and carburetted hydrogen gases, the alkali remaining in the state of carbonate, mixed with charcoal. This process was formerly employed to obtain carbonate of potash : the super-tartrate was exposed to a red heat in a crucible, and the residual matter was lixiviated with water, and then evaporated : and it has been supposed, that it affords the alkali purer than as it is procured by other processes. The watery solution of the super-tartrate decomposes gradually, and leaves the alkali in excess.

From the tendency of tartaric acid to form ternary combinations, super-tartrate of potash unites with a number of bases. It thus forms with soda and ammonia ternary compounds. Thenard has found, that it may even admit certain proportions of lime, barytes, or strontites; for although when large quantities of these earths are brought to act upon it, they decompose it and abstract the tartaric acid, when they are added in a state of solution in small quantity, they occasion no decomposition, but enter into combination with its principles; the liquid remains transparent, nearly to the point at which the acid of the super-tartrate is saturated; and if this be not exceeded, there are formed on the sides of the vessel, transparent crystals, in which analysis detects the presence of the acid, the alkali, and the earth that has been added. Magnesia and alumina enter into similar combinations, but form compounds which are not crystallizable *.

A singular effect produced on it by borax, or even by pure boracic acid, is, that of increasing its solubility in water, one part of borax, and three of super-tartrate, forming a compound so soluble, as to require not more than its weight of water to dissolve it; and one part of boracic acid, with four parts of the super-tartrate, being soluble in less than its weight of water. This is owing to the affinity of the two acids, according to Thevenin, who found, that when the boracic acid merely moistened is heated with 3 parts of tartaric acid, they become liquid, and the mixture, though solid when cold, is highly deliquescent. This, however, is denied by Vogel. The two acids, he affirms, do not unite: and the effect, therefore, must be owing to the relation of boracic acid to super-tartrate of potash. The ternary compound they form is very intimate, so that even the stronger acids decompose it very imperfectly †.

It acts on several of the metals, dissolves their oxides, and forms triple combinations; and its energy in this respect is so great, that Gay Lussac has considered it as acting the part of a simple acid. It dissolves oxides, which the tartaric acid alone does not dissolve.

According to Thenard's estimate of the composition of super-tartrate of potash, it consists of 57 of acid, 33 of alkali, and 7 of water. The crystals found in the shops con-

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* Nicholson's Journal, 4to, vol. v. p. 268.

† Annales de Physique et Chimie, tom. iii. p. 274. tom iv. p. 395.

tain, according to Vauquelin, about .007 of tartrate of lime; the crude tartar contains of the same earthy salt .016.

Tartrate of soda crystallizes in fine needles, or in thin plates: it is soluble in water, but if combined with an excess of acid, its solubility is diminished.

Tartrate of potash and soda has been long used in medicine under the name of Rochelle Salt. It is prepared by saturating the excess of acid in the super-tartrate of potash, by adding carbonate of soda: the liquor is strained, and, on evaporation and cooling, affords regular crystals, rhomboidal six or eight sided prisms, hard and transparent. They are permanent in the air, soluble in about five parts of cold water, and in less warm water, and consist, according to Vauquelin, of 54 of tartrate of potash, and 46 of tartrate of soda.

Tartrate of ammonia is a very soluble salt, which crystallizes in slender prisms. Tartrate of potash and ammonia, formed by saturating the excess of acid in the super-tartrate of potash by ammonia, crystallizes in hexaedral prisms acuminated by six planes.

The tartrates of barytes and lime are insoluble in water, but may be dissolved by an excess of acid. Those of magnesia and alumina, though soluble, are not crystallizable, their solutions becoming, on evaporation, viscid or gelatinous. Tartrate of lime consists, according to Berzelius, of acid 50.55, lime 21.64, water of combination 27.81.

Tartaric acid acts on those metals which decompose water so as to be oxidated; and it readily combines with the oxides of the others. Few of these combinations have been examined, or are of importance. The acid does not precipitate the solutions of gold, platina, or silver; but its salts do by double affinity. In the same way it may be combined with oxide of mercury, and forms an insoluble compound. It unites with oxide of copper, and forms a compound of little solubility, of a green colour. It acts on iron in its metallic state, and dissolves it with effervescence;

the solution, on evaporation, becomes gelatinous. On zinc its action is similar. It combines with the oxides of tin and lead, decomposing their solutions, and forming compounds of a white colour: tartrate of lead consists of 37.5 of acid, and 62.5 of oxide of lead. It precipitates the solution of bismuth of a fine white colour, forming a cosmetic known under the name of pearl white. It dissolves the oxides of antimony, forming a compound which crystallizes irregularly and without difficulty.

Ternary combinations can also be formed, by subjecting metals or their oxides to the action of super-tartrate of potash. Thenard has examined several of these *. The alkaline tartrates of manganese, iron, zinc, and tin, are very soluble, and are of difficult crystallization: they are not decomposed, either by the pure alkalis or alkaline carbonates, but are decomposed by sulphuretted hydrogen, the hydro-sulphurets, and the gallic acid. The alkaline tartrates of silver and of mercury suffer decomposition, not only from these agents, but likewise from the alkalis, either pure or in the state of carbonate. The alkaline tartrate of lead is not soluble; that of copper is distinguished by its saccharine taste, and the great quantity of metal which it contains. The tartrate of potash and antimony is by far the most important of these combinations: it is the substance which has been long used in medicine under the name of Emetic Tartar, and which is superior to the other antimonial preparations, in the certainty of its operation. The method of preparing it and its properties, have been taken notice of under the history of antimony.

Tartaric acid, in its pure state, is not applied to any use; of its combinations, some are employed in the practice of medicine.

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* Nicholson's Journal, 4to, vol. v. p. 269.

The acid which distils over when tartaric acid is decomposed by heat, differs in its properties from that acid. It was formerly regarded as a peculiar one, and named Pyro-tartarous acid. Fourcroy and Vauquelin examined it, as well as the empyreumatic acids obtained from gum or sugar, or from wood, and which had been distinguished by the names of Pyro-mucous and Pyro-ligneous acids, and concluded that they are all acetic acid, slightly modified by the small portion of empyreumatic oil dissolved in them. Gehlen called this in question, and observed, that the pyro-tartarous acid, in particular, differs in its properties from the acetic; it leaves, on evaporation, a crystallized residuum, a property which the acetic does not exhibit. Fourcroy and Vauquelin again submitted it to examination, and found reason to admit the conclusion of Gehlen. The acid procured by the first distillation from tartar is mixed with oily and resinous matter, from which it may be freed by saturating it by carbonate of potash, evaporating to dryness, re-dissolving the salt several times in water, and at length decomposing it by diluted sulphuric acid with a gentle heat. An acid liquor distils over, which has only a slight smell of acetic acid, and an acid salt sublimes, which adheres to the neck of the retort in white scales. This is the Pyro-tartaric acid. Its taste is extremely sour; the crystals melt readily, and evaporate in white fumes when placed on a heated body; they dissolve copiously in water, and crystallize by spontaneous evaporation; their solution does not, like that of tartaric acid, precipitate nitrate of silver or acetate of lead, but it precipitates nitrate of mercury; nor does it form with potash a salt with an excess of acid of sparing solubility; and its neutral compound with potash does not precipitate the salts of barytes or of lime. These chemical relations at once distinguish it from tartaric acid; while its inferior volatility, and its crystallizing by evaporation, distinguish it from acetic acid. The acid liquor which distils with it in its formation, yields by evaporation crystals having the same properties: it contains a little acetic acid, formed in the process. Pyro-tartaric acid is therefore a peculiar product of the decomposition of tartaric acid by heat *.

SECT. XXV.—OF BENZOIC ACID.

It has been remarked, in treating of the balsams, that they afford a peculiar acid, on the application of heat. The concrete balsam, named Benzoin, being that from which it is usually procured, it has received the name of Benzoic Acid.

A quantity of benzoin being reduced to coarse powder, is put into an earthen matrass, to the mouth of which a paper cone is adapted; a moderate heat is applied; the acid is volatilized in white vapours; these condense in small brilliant crystals, which, when the sublimation is slow, appear in the form of slender prisms. The paper cone is changed as it becomes warm, a new one is applied, care being taken not to raise the heat too high, as then a quantity of oily matter is volatilized, by which the acid is coloured brown. If, however, the heat be raised fully, and applied as long as any product is volatilized, a method recommended by Chaptal, a larger quantity of benzoic acid is obtained than by any other process: and the acid may be purified by repeated solution and crystallization.

Geoffroy found that this acid might also be abstracted from benzoin by the action of boiling water; the water,

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* Nicholson's Journal, vol. xxvi. p. 44.

after having been boiled on the benzoin in powder, affording crystals of the acid on cooling. Scheele proposed another method of obtaining it in the humid way. Four parts of benzoin in powder, and one part of slacked lime, are mixed with 24 parts of water, and boiled for half an hour. The benzoic acid combines with the lime, and forms a compound soluble in water. The undissolved matter is allowed to subside, and the liquor when clear is poured off: a fresh quantity of water is boiled on the residuum, and the ley thus obtained is added to the former; and this is repeated for a third time. The whole is reduced by evaporation, and to the concentrated solution there is to be added muriatic acid, until it be sensibly acid; the muriatic combines with the lime; and the benzoic acid being insoluble in cold water is precipitated in a powder of a brownish colour: this is washed with a little water, is dissolved in boiling water, and, as the solution cools, crystals of benzoic acid form. About 14 drachms are obtained by this process from one pound of benzoin. Gren introduced a slight modification of it, by boiling the benzoin with carbonate of soda, and adding to the filtered liquor diluted sulphuric acid, so as to precipitate the acid of benzoin; this is rather more economical, from sulphuric being less expensive than muriatic acid.

Mr Brande states the following as the quantities of acid, obtained by these processes, from one pound of benzoin,

	oz.	dr.	scr.	gr.
By Scheele's, - -	1	6	2	19
— Chaptal's, - -	2	0	0	0
— Geoffroy's, - -	1	0	0	10
— Gren's, - -	1	5	1	10*.

It has been observed, under the history of the balsams, that there is reason to conclude the benzoic acid is not formed, as some have imagined, but is merely extracted in these processes. Mr Hatchet found, however, what seems to favour the former opinion, or at least leads to the conclusion that the quantity of acid is increased by a new formation of it, that the balsams, when they had been mixed with sulphuric acid, afforded a considerable quantity of benzoic acid by sublimation, and that some, as dragon's blood, afforded it when subjected to this treatment, which did not afford it when exposed to heat alone *. But it is not improbable that the acid may facilitate its separation, by its action on the resinous matter, and perhaps by preventing the formation of empyreumatic oil, so as to allow of the heat being raised higher, or applied for a longer time.

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* Nicholson's Journal, vol. x. p. 88.

Benzoic acid is formed in the animal system. It is found in the urine of the horse, cow, and other gramenivorous animals. Fourcroy supposed, that it is derived from some of the grasses on which these animals feed. It is also sometimes found in the urine of children, and in general is present when phosphoric acid is deficient.

Benzoic acid is, according to the method in which it has been obtained, in soft flakes, or in slender needle-like crystals, frequently of considerable length; when pure, white and brilliant. Its taste is pungent, and slightly acidulous. It has a peculiar odour, somewhat aromatic, and which becomes strong when it is heated and volatilized. From the experiments of Giesse, this odour appears to be adventitious, benzoic acid having been obtained by him inodorous, without any of its other qualities being changed, by combining the acid with a solution of potash, and precipitating it by muriatic acid. On each repetition of this experiment, the odour diminished, and, after the third, it had entirely disappeared. Another method, equally successful, was to dissolve the odorous acid in as small a quantity as possible of alkohol: to drop into the solution water until the acid was precipitated: when dried by a gentle

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* Philosophical Transactions, 1805.

heat, it was found to be inodorous ; the small quantity of oily matter derived from the balsam to which its odour is owing remaining combined with the alkohol *.

This acid is volatilized by a very moderate heat ; its vapour is acrid and suffocating ; it is also fusible. Heated on burning fuel, it inflames. Urged with a strong fire in close vessels, the portion that is not immediately sublimed is decomposed, and affords an acid liquid ; a quantity of oil more abundant than what is produced in the decomposition of any other vegetable acid ; and carburetted hydrogen in considerable proportion ; a small quantity of charcoal is left in the retort. This decomposition is more completely effected when the volatilization of the acid is retarded by mixing it with sand ; or by combination with a base. From the products of its combustion, in the mode employed by Berzelius in the analysis of vegetable substances, he inferred, that it consists of carbon 74.41, oxygen 20.43, hydrogen 5.16 †. But as he operated upon it in the state of benzoate of lead, in which state there is the abstraction from it of a portion of water, (what Berzelius considered as the water of composition), there are to be added the proportions of oxygen and hydrogen equivalent to this. And, from the estimate of the quantity of water, this gives as the proportions, carbon 74.41, oxygen 27.43, hydrogen 6. This is the only case in which the proportion of oxygen to carbon is even less than the lowest of the definite proportions, in which there is reason to believe otherwise these elements unite. The hydrogen is almost precisely that of the first definite proportion to carbon. The analysis, however, must be considered as imperfectly determined, Berzelius himself admitting, that from the volatility and weak affinity of the acid, it is attended with more difficulty than any other.

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* Philosophical Magazine, vol. xiv. p. 331.

† Annals of Philosophy, vol. v. p. 182.

It is sparingly soluble in cold water. According to Wenzel, 400 parts of cold water are required for dissolving one part of it; while the same quantity of boiling water can dissolve 20 parts of it, 19 of which separate by crystallization on cooling. Bucholz states, however, that 200 parts of water dissolve it at the common temperature, and it dissolves in 24 parts of water. Its hot solution reddens litmus. Alkohol dissolves about half its weight of it, and when hot an equal weight: it is precipitated by the addition of cold water.

Benzoic acid is not easily decomposed by the mineral acids. Sulphuric acid dissolves it; and, on the addition of water, the benzoic acid is separated, little altered. Nitric acid dissolves it, and water separates it from this solution unaltered; but if the acid be distilled from it, it suffers, according to Hermbstaedt, some chemical change.

This acid unites easily with the alkalis and earths. Its salts are named Benzoates.

Benzoate of potash is obtained in acicular crystals, which are soluble in water and deliquescent. Benzoate of soda is soluble and crystallizable, but, according to Bergman, does not deliquesce. Benzoate of ammonia is possessed of the same properties; is volatile, and easily decomposed. Benzoate of barytes is likewise soluble, and crystallizes without difficulty. Benzoate of lime crystallizes in brilliant plates, and is soluble in about 20 parts of cold water. The benzoates of magnesia and argil are soluble, crystallizable, and deliquescent.

The combinations of benzoic acid with the metals have been made the subject of experiment by Trommsdorff. He boiled, either on the metal in filings, or on its oxide, the acid of benzoin, with as much water as was sufficient for its solution: With oxide of gold, a solution was obtained which shoots into irregular crystals, permanent in the air, soluble with difficulty in water, and scarcely at all so in alkohol. The oxide of silver is scarcely dissolved; but a benzoate of this metal is obtained, by adding benzoate of potash to a solution of nitrate of silver; a precipitate is thrown down, which is soluble in hot water, but precipitates again on cooling, and which, like the other salts of silver, is blackened by light. The solution of oxide of platina affords minute aggregated crystals, permanent in the air, difficultly soluble in water, and insoluble in alkohol. The solution of oxide of quicksilver affords by evaporation a white brilliant mass, somewhat soluble in alkohol, but not sensibly soluble in water. Oxide of copper is easily dissolved by the acid, and a solution obtained, which shoots into small pointed crystals of a dark green colour, difficultly soluble in water, and insoluble in alkohol. Oxide of tin is not dissolved. Lead is somewhat eroded, and its oxide is dissolved, forming a solution of a sweetish taste, which shoots into white shining crystals, soluble both in water and in alkohol: when formed by precipitation, benzoate of lead is a light crystalline powder, slightly soluble in water, and fusible. Iron is dissolved in small quantity: the solution obtained from the oxide affords crystals of a yellow tinge, having a sweet taste, which are soluble in water. Benzoate of iron, formed by adding a solution of benzoate of ammonia to a solution of a salt of iron, is nearly insoluble; and its precipitation has hence been employed as a test to discover iron, being less expensive than succinate of ammonia: like this test too, it serves to separate iron from manganese and other metals, these not being precipitated by it: the solution of iron requires to be at the maximum of oxidation, and also neutral; the benzoate collected by precipitation, and dried by exposure to the air, contains .025 of red oxide of iron *. The benzoate of ammonia affords the best form of thus applying benzoic acid as a precipitant, as the acid itself is too sparingly soluble; and the other benzoates are in their evaporation

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* Philosophical Magazine, vol. xl. p. 251. 258.

liable to lose a portion of acid, and thus to exist with an excess of base, the action of which would introduce a source of error. The solution of oxide of zinc by benzoic acid has a styptic taste, and yields arborescent crystals, which are soluble both in alkohol and water. The solution of oxide of bismuth yields a light mass, composed of white crystalline spiculæ, easily soluble in boiling water, and sparingly soluble in alkohol. Oxide of antimony affords a solution which does not crystallize, but, on evaporation, gives a white flaky mass, soluble in water and in alkohol. White oxide of manganese is dissolved by the acid boiled on it, and, by evaporation, small scaly crystals are obtained, abundantly soluble. Oxide of nickel gives a solution of a pale green colour, which does not crystallize. The solution of oxide of cobalt affords crystals of nearly the same figure as the acid itself. The solution of oxide of arsenic gives plumose crystals, which effloresce in the air, are soluble in hot water, and crystallize on cooling *.

With the exception of being employed as a test of iron, benzoic acid is applied to no use. It was formerly employed in the practice of medicine, and still enters into one or two officinal preparations; but does not appear to have any medicinal virtue.

SECT. XXVI.—OF ACETIC ACID.

This acid exists, as has already been remarked, in the sap of vegetables, combined with potash and lime, and is sometimes also present in excess. It is discovered by evaporating the sap, and adding to the solid matter sulphuric acid: the vapours of acetic acid are then perceived by

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* Crell's Chemical Journal, vol. iii. p. 11.

their smell. It is more peculiarly, however, the produce of fermentation, and the production of it even characterizes one stage of that process. It is under it, therefore, that its chemical history is best placed.

SECT. XXVII.—OF PRUSSIC ACID.

THE acid to which this name has been given, is usually obtained in the decomposition of animal substances by heat, being formed by new combinations of the elements of animal matter. But it has been discovered, that it exists also as a product of the vegetable system. It had always been observed, that it has in a high degree the peculiar fragrant smell of peach blossoms; and it has also been observed, that the same smell is perceptible in the distilled waters from the leaves of the cherry-laurel, the fruit of the bitter almond, and some similar vegetables, all of which are narcotic. Bohn at length found, that when potash is added to the water distilled from the bitter almond, it acquires the property of forming a blue precipitate with solutions of iron,—the sure indication of the presence of prussic acid. Schroeder confirmed this, and found farther, that the same acid is contained in the distilled waters of the peach blossom and the cherry-laurel, so that even a prussiate might be obtained from them crystallized, by distilling them from potash. These singular results were confirmed by Vauquelin and by Bucholz. The latter chemist succeeded in separating prussic acid from the essential oil of the cherry-laurel, by agitation with solution of potash. And Roloff has since shewn, that lime-water, and water of ammonia, with the latter of which Bucholz did not succeed, abstract the prussic acid from the same oil, as well as from the oil of the bitter almond *. Vogel too has found, that the residue of the bitter almond after expression, yields prussic acid by distillation with water. And this acid has in a high degree the narcotic property of the vegetables in which it is thus found. Prussic acid therefore may be classed with the vegetable acids; but as it is more peculiarly formed from animal matter, and is more analogous in composition to animal substances, its history will be afterwards delivered.

SECT. XXVIII.—OF MOROXYLIC ACID.

THIS name was given by Klaproth to an acid which he extracted from a saline efflorescence, found by Mr Thomson on the trunk of the white mulberry (Morus alba), in the botanical garden at Palermo. The examination of it was imperfect, from the smallness of the quantity obtained by Klaproth; but as he regards it as a peculiar acid, it is necessary to give it a place, though farther investigation may connect it with one or other of the acids already known. In its properties it approaches to succinic acid.

The saline exudation consists of this acid in combination with lime, mixed with extractive matter. It is of a brown colour; approaches to succinic acid in its taste; swells when placed on burning fuel, and emits an acrid vapour, leaving an earthy residuum. By solution in water, and crystallization, the saline matter is obtained more pure, and of a lighter colour. The alkaline carbonates precipitate lime from its solution. Exposed to heat, it

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* Journal de Physique, tom. li. p. 165. 179. tom. lvi. Annales de Chimie, tom. xlv. Philosophical Magazine, vol. xviii.

gives the usual products of vegetable matter; and leaves a residuum of charcoal and lime.

The pure acid was obtained from this salt by two processes. In the first, to a solution of the salt a solution of acetate of lead was added: the precipitate formed, consisting of the acid with oxide of lead, was mixed with sulphuric acid, diluted with three times its weight of water. Sulphate of lead was formed, and the filtered liquor, by evaporation, afforded the moroxylic acid, in needles of a pale straw colour. In the second, the salt was decomposed by sulphuric acid, the sulphate of lime separated, and the pure acid obtained.

This acid resembles succinic acid in taste. It remains dry on exposure to the air, and is soluble both in water and in alkohol. When heated in a retort, a small quantity of acid liquor is obtained: a concrete salt next rises, which condenses in prismatic crystals, colourless and transparent; a little charcoal remained in the retort. These are soluble in water, and the solution affords, by spontaneous evaporation, colourless crystals. It appears, therefore, that sublimation is the best mode of obtaining this acid free from the extractive matter which adheres to it. In its pure state, it did not precipitate the metallic solutions, as the native salt does from which it is extracted *.

SECT. XXIX.—OF MORPHIN.

SOME years ago Derosne, a French chemist, announced the discovery of a peculiar principle in opium. He obtained it by digesting water on crude opium, evaporating the solution, and digesting the precipitate which falls down

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* Nicholson's Journal, vol. x. p. 129.

during the evaporation in alkohol. As the spiritous solution cools, the peculiar principle of the opium precipitates in crystalline grains. These are purified by repeated solution and evaporation; and a substance is thus procured in prisms, of a white colour, free from taste or smell; sparingly soluble in hot water, insoluble in cold water; soluble in alkohol, and precipitated from this solution by water; soluble also in ether; dissolved likewise by the acids as well as the alkalis, the solutions in the acids being precipitated by the alkalis, and those in the alkalis by the acids; decomposed by nitric acid, so as to afford oxalic acid; and decomposed after fusion by heat, affording the usual products of the decomposition of vegetable matter, with ammonia. He also remarked, that when precipitated from the solution of opium by the alkalis, it retained, even in its crystallized state, the power of changing the colour of violet to a green; but he ascribed this to the alkali employed in the precipitation. This substance Derosne found to act as a powerful narcotic on the living system, and he regarded it as the principle in which the narcotic quality of opium resides *.

Sertuerner, a German chemist, had been occupied about the same period with the analysis of opium, but obtained very different results. Not considering his researches as altogether accurate, he continued the investigation; and lately he has announced the discovery of a principle in opium which differs essentially from that described by Derosne. It has the characteristic chemical properties of an alkali, and being composed of the usual elements of vegetable matter, is to be considered as an alkali having a compound radical, bearing in this respect the same analogy to the other alkalis, that the vegetable acids do to the other acids. It exists, according to this chemist, in opium in combination with a peculiar acid, which he has

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* Annales de Chimie, tom. lxv.

named Meconic acid; and this combination, he affirms, constitutes the substance obtained by Derosne. From its narcotic power, he has given it the name of Morphium, or Morphine. The following account of its properties is taken from his Memoir *.

To obtain it, eight ounces of dry opium were digested with heat, in successive portions of distilled water, until it was no longer coloured. The liquors being evaporated, an extract was obtained, which was turbid when diffused in water, but with the assistance of heat, or a larger quantity of water, formed a transparent solution. On adding to this solution an excess of ammonia, a substance is precipitated of a greyish-white colour, which forms into small irregular transparent crystals. These, after being washed repeatedly with water, are the morphin, combined with a little extractive matter and meconic acid. This substance was saturated by sulphuric acid diffused in water, and added in slight excess; was precipitated anew by ammonia, and submitted repeatedly to the action of that alkali, to separate the extractive matter. But as that was only imperfectly attained, it was washed repeatedly by alkohol, which acquired colour from it deeply, and the morphin remained nearly colourless. To obtain it in a state of perfect purity, it was dissolved repeatedly in alkohol, and crystallized, and was thus procured in colourless prisms †.

Pure morphin has the following properties: It is co-

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* Annales de Chimie et Physique, tom. v. p. 21.

† In an appendix to the Memoir, the following process is given, differing somewhat from that above. Rub eight ounces of opium in powder, with two or three ounces of concentrated acetic acid, and a little distilled water: diffuse the paste in two or three pounds of cold water, and strain the liquor: it contains acetate and meconate of morphin, with extractive matter. Precipitate the morphin by ammonia, and evaporate the liquor to one fourth; separate the morphin after cooling by filtration.

lourless; soluble in boiling water in a small proportion; very soluble in alkohol and ether, especially with the aid of heat; the taste of its solutions is extremely bitter. Both the watery and spiritous solutions render brown the yellow colour of rhubarb, and this more strongly than that of turmeric; they restore the colour of litmus, which has been reddened by an acid; nor is this owing to the presence of ammonia, for the morphin produces the effect when no ammonia is present. It dissolves easily in the acids; and forms neutral salts, distinguished by very characteristic properties. The following are enumerated:

The sub-carbonate of morphin is formed in causing carbonic acid to act on morphin, or in decomposing its solution by sub-carbonate of potash. The carbonate crystallizes in short prisms. The acetate exhibits a radiated crystallization, and is very soluble. The sulphate is also very soluble, and affords crystalline ramifications. The muriate gives a feathery crystallization; it dissolves with more difficulty than the other salts, and assumes on cooling, if the evaporation is pushed too far, a brilliant mass, of a silvery-white colour. The nitrate exhibits a diverging radiated appearance. The tartrate crystallizes in prisms; and the sub-meconate displays a similar crystallization. All these salts are sufficiently soluble in water, have a micaceous lustre, and effloresce quickly when exposed to the air. They all appear to be extremely deleterious.

In the order of salifiable bases, morphin ranks after ammonia, as it is disengaged from all its combinations by that alkali. It occupies the lowest place among the alkalis, having the least alkaline energy, and not having the property of forming soaps with oils. It has a less strong attraction to the acids than ammonia, and even than magnesia; but it decomposes the greater number of the metallic salts, such as sulphate, muriate, and acetate of iron; and different salts with a base of mercury, lead, and copper. It destroys the green colour of acetate of copper, forming with it probably a ternary combination. It combines with the carbonic acid of the atmosphere.

Morphin melts easily from heat, and then resembles melted sulphur; it crystallizes on cooling. It burns strongly, and when heated in close vessels, it affords a black resinous-like substance, having a peculiar smell. It combines with sulphur by the aid of heat, but at the same moment is decomposed, forming hydro-sulphuric acid, (sulphuretted hydrogen). Its elements may be presumed to be oxygen, carbon, and hydrogen, with probably nitrogen. Galvanic electricity produces little effect on it, even in contact with a globule of quicksilver; the quicksilver, however, seemed to change its consistence, and increase in size.

According to Sertuerner, the morphin exists in opium in combination with an acid, which he has named Meconic,—an inference so far probable, as the watery solution of opium is sensibly acid. The liquid from which morphin had been precipitated by ammonia, containing this acid, was evaporated to the consistence of syrup; a portion of that principle separated from it, and was also precipitated by a farther addition of ammonia, but was redissolved by the extractive principle, on expelling the ammonia by heat. On pouring into the solution muriate of barytes, a precipitate was formed, which he considered as a quaternary compound of barytes, meconic acid, morphin, and extractive matter. He endeavoured to abstract the two latter by the action of alkohol, to saturate the barytes by sulphuric acid, and obtain the meconic acid pure. He procured it by evaporation, but coloured; and to purify it he had recourse to sublimation. It melted at first in its water of crystallization, then sublimed and condensed in slender needles, colourless, of a sour taste, having all the properties of the stronger acids, and distinguished by its strong affinity to oxide of iron, which it precipitates from its muriatic solution of a fine cherry-red colour.

Morphin is described by this chemist as very highly narcotic, so that the most minute quantity only can be taken with safety; a grain even in divided doses, dissolved in alkohol, produces very violent effects. The meconic acid has no deleterious operation; and it seems even to diminish the activity of the other principle.

The principal facts stated by Sertuerner, particularly with regard to the properties of morphin, have been confirmed by Gay Lussac and by Robiquet *. The latter chemist, finding that when it was heated in a strong solution of potash, it gave some traces of ammonia, to obviate the supposition that its alkaline properties may arise from the presence of that alkali employed in its precipitation, substituted magnesia, boiling a small portion of this earth in a concentrated watery infusion of opium: the morphin was obtained perfectly pure, with all its characteristic qualities; it seemed even to be rather more alkaline than when it had been precipitated by ammonia: it contained no magnesia, and burned without affording any residue.

Robiquet could obtain the peculiar acid in opium only in very minute quantity by the process of Sertuerner. But he obtained it more copiously by boiling magnesia in excess with the aqueous solution of opium; treating the deposite with very dilute sulphuric acid; adding to the solution muriate of barytes, which precipitated sulphate and meconate of barytes, and decomposing the latter by sulphuric acid. The meconic acid may be procured, by evaporation of its solution, in crystals; which may be purified by sublimation by a very gentle heat. It is then obtained in white scales or needles: it is fusible by a moderate heat, somewhat superior to that of boiling water, and as soon as it melts it sublimes without decomposition: it is very soluble both in water and in alkohol; reddens litmus: it has not that marked action on oxide of iron which Ser-

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* Annales de Chimie et Physique, tom. v. p. 42. 275.

tuerner describes: it forms soluble salts with potash, soda, and lime. The salt of Derosne is not, according to Robiquet, the meconate of morphin, as Sertuerner had supposed; he regards it as a substance existing in opium along with morphin, but altogether independent of it. This is a question which must be regarded as imperfectly determined.

The alkaline powers of morphin appear to be established; and the discovery is important, as proving that these powers are not, as the analogy from potash, soda, the earths, and metallic oxides, would lead to conclude, exclusively the result of oxidation of a metallic base. It adds confirmation to the view I have proposed with regard to the theory of alkalinity, since, while ammonia, in opposition likewise to that analogy, is to be regarded as a compound of a simple radical not metallic, rendered alkaline by hydrogen, morphin may be regarded as composed of a compound radical rendered alkaline by the same element, alone, or in joint action with oxygen.

SECT. XXX.—OF LIGNIN OR WOOD. CORK. SUBERIC ACID.

WOOD is in every vegetable the basis to which the other principles are attached; the skeleton as it were of the plant, and the substance of which its vessels are formed. The bark, and the fibrous part of the leaves, are of a similar nature. The term Woody fibre has been applied to denote it, or the name Lignin may be given to it as a peculiar principle. It has every claim to be regarded as such, since it is possessed of properties sufficiently appropriate and distinctive.

Wood is fibrous in its texture, the fibres being interlaced. It is inodorous, insipid, and perhaps when perfectly pure is free from colour. It is however frequently possessed of colour, taste, and smell, from the presence of extractive matter, mucilage, resin, or essential oil. It is only when these have been extracted by the action of water and alkohol, that the wood can, as a chemical principle, be regarded as pure. A fibrous matter often pulverulent, remains after this operation, and it is from this that its characters must be derived.

The ligneous fibre is insoluble in water: even when the water is boiled on it, it is not dissolved. It is equally insoluble in alkohol: hence it forms the residuum, when the solid parts of plants have been acted on by these fluids.

From exposure to the air in a dry state, it does not appear to suffer any change; but when humid, it is gradually decomposed, and passes through various intermediate states to that of a black mould, consisting principally of carbon. Saussure found, that the oxygen of the atmospheric air is, during this change, consumed, and that it is replaced by an equal volume of carbonic acid gas; and he concludes from his experiments, that the oxygen abstracts part of the carbon of the wood, but that it loses at the same time a larger proportion of its oxygen and hydrogen, which form water; and that by the abstraction of these principles, the proportion of carbon is increased in the residual matter. When the air is excluded, and the influence of water alone admitted, the changes are different, and the proportion of carbon is rather diminished than increased *. It is known too, that when the air is entirely excluded, wood decomposes with extreme slowness, even though humid, as, for example, when it is buried in the earth.

According to the same chemist, water boiled on wood does not merely dissolve its extractive matter, but forms a

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* Recherches Chimiques, p. 148.

portion of it, so that it is impossible to reduce wood by repeated decoctions to such a state that it shall not afford it. He boiled three ounces of oak saw-dust in twenty-four times its weight of water, poured off the decoction, evaporated it, and repeated this a number of times. The quantity of matter afforded by the first decoction was 90 grains; that by the second 29 grains. It continued to diminish to the ninth decoction: the eleventh and twelfth afforded the same quantity as the ninth, amounting to 4 grains. The remaining saw-dust was exposed to the air for two months. On being submitted to a new decoction, it gave 5½ grains of extract; the fourteenth decoction afforded 4 grains; and after a new exposure for two months to the air, the quantity was again augmented to 5½ grains. Wood, the most completely freed of its soluble principles, furnishes always by maceration in water with the contact of air, infusions holding extractive matter dissolved *.

The alkalis act on wood: when an alkaline solution is allowed to remain over wood, it receives colour, and the colour of the wood is darkened. With the assistance of heat, they soften, and partly dissolve and decompose it.

The stronger acids act on it. Sulphuric acid chars it, rendering it in a short time black and soft. Nitric acid gives it a yellow tinge; and when acting on it in large quantity, disengages, according to Fourcroy, nitrogen gas, and converts it into oxalic acid, with small quantities of malic and acetic acids.

When wood is exposed to heat in an iron retort, a portion of water distils over, which, as the distillation proceeds, becomes acid, and at length a liquor very acid and pungent, of a yellow colour, is condensed; an empyreumatic oil passes over in considerable quantity: carburetted hydrogen and carbonic acid gases are disengaged; and a portion of ammonia is produced, which exists neutralized

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* Recherches Chimiques, p. 150.

in the acid liquor. A concrete charcoal remains, which retains the figure, and in some measure the texture of the wood. The acid procured in this process, was formerly regarded as a peculiar one, and named Pyro-ligneous Acid. The researches of Fourcroy and Vauquelin shewed, that it is diluted acetic acid, with an impregnation of empyreumatic oil. It is afforded in so large a quantity, that the process is employed to furnish this acid, for some of the purposes to which it is applied; and for chemical preparations it has the advantage over common vinegar, of being free from malic or tartaric acid. In preparing charcoal for the fabrication of gunpowder, the wood being distilled in iron retorts, the acid liquor is collected, and is used by the calico-printers to form the acetate of iron, which they employ as a mordant. It is also now purified by distillation from charcoal, and applied extensively to the purposes for which vinegar is used.

The charcoal of wood affords, after its combustion, a quantity of saline matter, principally carbonate and sulphate of potash and of lime, muriate of potash, and phosphates of magnesia and lime; and portions of earths and metals, particularly silex, iron, and manganese. All these, however, are not essential to the composition; the greater number are accidental, and, as has been already stated, (page 67.), often dependent on the soil, and derived from it. The portion of charcoal afforded by different woods, is different, being more as the wood is compact and dense: and the quantity of saline matter is different. On this subject, the researches of Saussure have been extensive; and his tables, which are too numerous to be inserted, present a number of facts on the incineration of different woods, the quantity of saline matter it affords, and the circumstances by which the production of this appears to be influenced.

When air is freely admitted, and the heat is raised to ignition, wood burns. Its combustion is at first vivid, or gives much light, from the extrication of the hydrogen in combination with a part of its carbon; but as this is dissipated, there is only the red glow of the charcoal. The products of the combustion are principally carbonic acid and water; and if nitrogen be a constituent principle of wood, as its analysis by heat appears to prove, ammonia is probably also evolved. An ammoniacal salt is accordingly found in the soot of fuel.

From the analysis of wood, it appears to consist of carbon, hydrogen, oxygen, and nitrogen, with probably lime. Of all the vegetable principles, it contains the largest proportion of carbon; since, independent of the quantity of this principle disengaged in the state of carbonic acid and other elastic products, the residual charcoal amounts to one fourth or fifth of the weight of the original wood. From this predominance of carbon, it probably derives its solidity, and its inactivity as a chemical substance. The proportions of its constituent parts have been given by Gay Lussac and Thenard, as determined by their mode of analysis by hyper-oxymuriate of potash. Oak wood afforded of carbon 52.53, oxygen 41.78, hydrogen 5.69; beach wood, carbon 51.45, oxygen 42.73, hydrogen 5.82.

Cork is a substance analogous to wood. It is the external bark of the Quercus suber; but, as Fourcroy observed, the epidermis of all ligneous vegetables is similar; and they are probably all varieties of the matter which constitutes the ligneous fibre.

Cork is light, soft, spongy, and elastic: it is inflammable; affords a little ammonia by distillation; and is acted on by chemical agents, in nearly the same manner as wood.

The principal peculiarity with regard to it, is that of affording an acid different from every other, when acted on by the nitric acid. This was first observed by Brugnatelli;

the production and properties of this acid, named the Suberic, have been more fully investigated by Bouillon Lagrange[*]; and by Chevreul[†].

The process employed to obtain it, consists in pouring on cork in a retort, six times its weight of diluted nitric acid, and distilling it from it with a gentle heat: red vapours are extricated; the cork swells and becomes yellow; and as the distillation proceeds, a soft spongy matter rises to the surface. The distillation is continued, until the vapours cease, (and to render the action more complete, the acid which distils over, may be returned upon the residual matter, and distilled again): the whole, while warm, is poured into a glass or porcelain bason, placed on a sand-bath, and a moderate heat is applied, stirring the matter constantly with a glass rod. It is thus gradually thickened: and as soon as it ceases to disengage white irritating vapours, the vessel is removed from the sand-bath, and the residual mass is agitated until nearly cold. A substance is obtained, of the consistence of honey, of a yellow colour, and a sharp penetrating odour when it is warm, an aromatic odour when cold. To obtain the acid which is contained in it, twice its weight of distilled water is heated upon it, and the solution is filtered from the part that is not dissolved by the water. It is of an amber colour, and has a smell approaching to that of prussic acid: on cooling it becomes turbid; the precipitate is separated by filtration, and the acid is obtained more pure. By evaporation and cooling, the suberic acid is deposited: the residual liquor, according to Chevreul, contains oxalic acid, and what has been named the Bitter Principle. In this operation the production of the acid is owing to the communication of oxygen from the nitric acid to the principles of the cork; carbonic acid gas is disengaged during the operation, along with the nitrous vapours. The matter deposited during the formation of the acid, consists principally of a substance which assumes the consistence of wax, and of a white tasteless powder, which has some analogy with fecula.

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[*] Annales de Chimie, tom. xxiii. p. 42.

[†] Nicholson's Journal, vol. xxiii. p. 149.

Suberic acid obtained by this process is coloured, but it may be purified by repeated solutions in water, by boiling with charcoal, or by combining it with an alkali, and precipitating by an acid. It is thus obtained, according to Chevreul, white as starch, particularly by precipitating it from its combination with lime by muriatic acid : it is not crystallizable : it is either pulverulent when precipitated, or when obtained by evaporation is in thin irregular pellicles. Its taste is slightly acid : dissolved in a small quantity of boiling water, it is irritating to the throat, and excites coughing. It reddens the vegetable colours, and it attracts a little humidity from the air. Exposed to heat, it is fused, then volatilized, and forms crystalline flakes on the sides of the vessel, and it yields vapours with boiling water, which condense in crystalline needles. Heated by the blow-pipe, it first liquefies, then becomes pulverulent, and lastly is sublimed, exhaling an odour of sebacic acid. It becomes brown from exposure to light.

At the temperature of 60°, an ounce of water dissolves 10 grains of the concrete acid, but if it is very pure, not more than 4 grains. Boiling water dissolves half its weight. According to Chevreul, one part of it requires for its solution 38 parts of water at 140°, and 80 parts at 55. It is also soluble in alkohol.

It is not altered by oxygen gas. The mineral, or vegetable acids, have little action on it, and do not completely dissolve it. Nitric acid does not decompose it.

Suberic acid unites with the alkalis and earths. Its salts are named Suberates. It does not precipitate barytes, strontites, or lime, from their saline combinations. The mineral acids in general precipitate the suberic acid from their solutions; and its salts are decomposed by solutions of almost all the metallic salts.

Suberate of potash crystallizes in four-sided prisms; has a bitter saline taste; is fused and decomposed by heat; and very soluble in water. Suberate of soda does not crystallize: its taste is slightly bitter; it is very soluble in water, and attracts humidity from the air. It is also soluble in alkohol. Suberate of ammonia has a saline bitterish taste: it is crystallizable; is very soluble in water; attracts a little humidity from the air, and is volatilized when heated before the blow-pipe. Suberate of barytes is not crystallizable, and is scarcely soluble in water, except from excess of acid. Suberate of lime is very sparingly soluble in water: boiling water dissolves a portion of it, but the greater part precipitates on cooling; nor does it crystallize; it is perfectly white; its taste is a little saline. Suberate of magnesia is in the form of a powder; it has a bitter taste; attracts a little humidity from the air; is soluble in water, and is decomposed by heat. Suberate of alumina cannot be obtained in a crystalline form, but is reduced by evaporation to a dry mass, of a yellow colour, transparent, having a styptic bitterish taste.

Suberic acid has no action on platina, gold, or nickel; but it forms salts with the other metals, which in general do not crystallize, and have a tendency to form with an excess of acid. It decomposes acetate and nitrate of lead, and nitrates of mercury and silver: with nitrate of copper it forms no precipitate, but the blue colour of the solution passes to green, as does also that of sulphate of copper: the solution of sulphate of iron becomes of a deep yellow, and that of sulphate of zinc of a clear golden yellow.

A character mentioned by Lagrange as peculiar to it is, that when a few drops of it are added to a solution of indigo in sulphuric acid, it causes the blue colour to pass to a green. According to Chevreul, however, this does not belong to the pure acid, but is owing to the presence of the bitter principle, the yellow colour of which renders the blue of the indigo green.

Bouillon Lagrange has observed, that this acid is distinguished from the citric by not crystallizing; from the gallic, by not precipitating iron black; from the malic, by being obtained in a concrete form; from the tartaric, by its volatility; from the oxalic, by not precipitating the solution of sulphate of copper, and by yielding to it lime. From these, and the phenomena presented in its combinations, he considers it as proved to be different from all the other acids.

The conclusion seems to be just. Yet it is to be observed, that it scarcely appears to have been obtained pure. A portion of extractive and bitter matter is formed along with it, which appears to be only partially abstracted, as is evident from the aromatic odour which alkohol developes in it, and from pure potash giving it a deep colour. We can scarcely, therefore, determine how far the peculiar properties it exhibits may be owing to the foreign matter combined with it. Chevreul appears to have obtained it in a purer state; he has remarked that it has a great analogy with the Sebacic acid; and that the only striking difference between them, is the crystalline form which the suberic acid assumes when dissolved in water or in alkohol.

Chevreul has since given the name of CERIN to a particular substance extracted from cork, by boiling it with alkohol under increased pressure. It is in small needles, as obtained from the solution, and white; it does not melt in boiling water, but softens; when heated or distilled, it suffers nearly the same changes as wax. The name of Cerin had been given by Dr John to that part of wax which is soluble in alkohol. How far these are similar is not determined*.

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* Annals of Philosophy, vol. ix. p. 58.

THE Ligneous Fibre is probably the basis of other vegetable productions, as of the fibres of flax, cotton, and other vegetables which are dressed and wove into cloth. They agree with it, not only in their natural production and their texture, but in chemical qualities; particularly in inflammability, insolubility in water or alkohol, and in the changes they suffer from the alkalis, the mineral acids, and other re-agents. Any differences they present are probably to be ascribed to their state of aggregation, or to slight modifications of composition. If this view be just, the basis of Paper must consist of the same principle, and it exhibits nearly the same chemical qualities.

SECT. XXXI.—OF COLOURING MATTER.

COLOURING MATTER. It has been supposed, that a principle exists in vegetables, in which their colour frequently resides, which has hence received the name of Colouring Matter. In this opinion there is a degree of obscurity and vagueness: colour being a secondary quality, which may reside in any species of matter, and which is exhibited by substances of the most opposite kind, there appears no reason to suppose, that there is a distinct principle to which it exclusively belongs. At the same time, there are many vegetable products, possessed of deep or of vivid colours, which agree in certain chemical relations: the colouring matter can be abstracted from them by the application of certain solvents; can be transferred from these to other substances exerting affinities towards it: and this, without the phenomena being always referable to actions exerted to any known proximate principle. In general, this colouring matter appears nearly allied to the extractive principle. Farther investigations must determine with more precision its varieties, and their relations to the other vegetable principles. At present, we so far generalize the facts on this subject as to state them in connection, without assuming that the principle to which they relate is uniform and distinct from every other. These facts are of importance from their connection with the arts of dyeing and pigment-making, of which, as being strictly chemical, it is necessary to take notice. Some also of these colouring substances, indigo in particular, are possessed of very distinctive properties.

The colouring matter of vegetables is usually mixed or combined with other principles. In this state it exists in the leaves, and flowers, in the bark, and in the wood of the stem and roots. It is extracted, and obtained more pure, by the action of those agents which are capable of dissolving it.

In many cases, water, cold or warm, is sufficient for this purpose. If logwood, brazil wood, madder, weld, or quercitron bark, be macerated in water, a coloured solution is obtained; and, by repeating the maceration with water, nothing remains but the ligneous fibre.

Sometimes the colouring matter is not soluble in water. It is frequently soluble in alkohol; and in a few substances, as in the alkanet root, is dissolved by oils essential or expressed. Frequently the extraction of the colour is facilitated by the action of the alkalis or acids; and some can be dissolved only by the aid of these. These differences prove, that this matter is not uniform, but that colour is attached to principles of a different nature.

When the colouring matter is in solution, it may be attracted from the solvent by other substances with which it enters into combination. There are some substances which appear in general to exert strong affinities to colouring matter, particularly alumina, and some of the metallic oxides. If alumina be boiled in a coloured infusion, it often happens that the colouring matter combines with it, and leaves the water of the infusion colourless. Or if alum be dissolved in a coloured infusion, and it be decomposed by the addition of an alkali, the earth in its precipitation attracts the colouring matter, forms a coloured precipitate, and if the due proportions have been observed, the liquid remains without colour. In like manner, if a coloured infusion be boiled with a metallic oxide, the colouring matter is often attracted by the oxide. Thus, Berthollet obtained combinations, by this process, of the colouring matter of logwood, and other dye-stuffs, with oxide of copper, and oxide of tin *. Or if certain metallic salts be dissolved in the infusion, and be decomposed by an alkali, the oxide in precipitating attracts the colouring matter. It is from similar affinities to the colouring matter that it is attracted by linen, cotton, silk, or wool, from its solutions; and even where the affinities of these are not sufficiently powerful, they may be rendered capable of attracting it, or the combination may be rendered more permanent, by their being impregnated with another substance, which has stronger attraction to it.

The shade of colour of any substance, and even the tint, are altered by chemical agents. The alkalis, acids, and various neutral and metallic salts, exert operations of this kind. By some the colour is weakened, or altogether discharged. Light, it is well known, proves injurious to the permanence and brightness of vegetable colours; so does exposure to the air; and the power of the oxymuriatic acid in destroying them is still more energetic.

On the principles now stated, rests in a great measure

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* Annales de Chimie, tom. i. p. 259.

the art of dyeing, the processes of which are arrangements founded on the affinities of colouring matter, in consequence of which colours are extracted, modified, transferred to the cloth, and rendered more permanent.

This view of the processes of dyeing, which reduces them to exertions of affinity between the colouring matter and the substance dyed, appears to have been suggested by Dufay. The theory adopted by the older chemists was rather mechanical. It was imagined, that the colouring matter was lodged in the pores of the cloth; and, according as these were more or less numerous, or of greater or less fineness, the cloth, or thread, would be more or less easily dyed; and the action of substances facilitating the dyeing, was supposed to depend on the changes they produced on this mechanical structure. This was the doctrine of Hellot. Dufay justly observed, that unless some species of attraction be exerted between the colouring matter and the substance receiving it, cloth immersed in a dyeing liquor could not receive a deeper colour than that of the liquor itself; whereas the liquor has always the deepness of its colour diminished, and, if certain proportions are observed, it becomes limpid, and the colouring particles are entirely transferred from it to the cloth.

Bergman gave this view, with more precision, referred the phenomena of dyeing entirely to chemical principles, and established this by experiment. In immersing wool and silk in a solution of indigo in sulphuric acid largely diluted with water, he observed, that the wool was speedily dyed, and that, if the proper proportions were observed, the solution was nearly or entirely deprived of colour. The silk was dyed more weakly; it only lessened the colour of the solution, but did not abstract it entirely. These phenomena he ascribed to the different forces of attraction exerted towards the colouring matter. In consequence of such an attraction, the sulphuric acid had dissolved the indigo; the silk exerted to the particles of the indigo a stronger attraction than the diluted acid: it therefore abstracted them from the fluid. And the wool did this more rapidly and completely, as having to these particles a still stronger attraction *.

The difference in the forces of affinity of the different materials of clothing for the various kinds of colouring matter are so considerable, that they vary, not only in the facility with which they are dyed, and the deepness of colour they assume from the same dyeing liquor, but frequently one will receive no colour from a composition which will give another a deep tinge. Cotton receives scarcely any colour in a bath in which wool is dyed scarlet. Wool appears to have the strongest attraction to colouring matter; next to it is silk, then linen, while cotton has the weakest, and is therefore dyed perfectly with most difficulty. Animal matter appears therefore to have a stronger attraction to the colouring particles than vegetable substances have; and this shews some analogy between colouring matter and tannin.

When the substance to be dyed has little or no attraction to the matter on which the colour depends, so as either not to be capable of abstracting it from its solvent, or of retaining it with such force as to form a permanent dye, there are certain arrangements by which colour is communicated and rendered permanent. These consist in impregnating it with some substance which shall serve as a bond of union between them. Such substances are, in the language of the art, denominated Mordants. Their use is essential in the processes of dyeing, and the discovery of them has been altogether empirical, or without any knowledge of the principles on which they operate. Macquer seems first to have given clearly the theory of their action: "where they have been used," he observes, "it is not the stuff immediately which takes the colour, but

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* Opuscul. vol. v.

the earthy or metallic part of the mordants; so that when stuffs are well dyed by these processes, it is owing to those coloured precipitates being capable of adhering to them more or less forcibly." Mordants, therefore, are substances which, on the one hand, have an attraction to the matter to be dyed, and, on the other, to the colouring matter, and which thus serve to unite them. Without their use, either the colouring matter would not be attracted, or be attracted so weakly, that in washing the cloth it would be again removed. The principal mordants are alum, acetate of argil, muriate of tin, sulphates of copper and zinc, acetate of copper, oxide of arsenic, tannin, and certain animal substances. Of those of the saline kind, it is not so much the entire salt, as its earthy or metallic base, that serves to fix the colouring matter; and in the course of the process, it is accordingly generally disunited from its acid. Hence the extensive application of alum and of the solutions of tin as mordants, from the powerful affinities of alumina and oxide of tin to colouring matter.

Sometimes mordants are employed rather to heighten the colour, or give it more brilliancy, or communicate a particular shade. Besides the substances already enumerated, the sulphuric and nitric acids, and even the oxymuriatic acid, in small quantity, are employed with this view.

Mordants are susceptible of a great variety of applications, with regard to the various dyes, and the different cloths; and the proper management of them constitutes a great part of the art of dyeing. They are used, either by previously impregnating the cloth with them, or by mixing them with the dyeing materials, or sometimes both methods are conjoined. There are also numerous varieties in the composition of the dyeing materials, a number of substances being often mixed, in order to procure a particular colour or shade. This evidently admits of no abridged account; and I must refer, therefore, for any details with regard to it, to the scientific treatises of Berthollet and Bancroft, on the Art of Dyeing. An experimental investigation of the principal mordants has also been undertaken by Thenard and Roard †.

The art of cloth-printing or calico-printing, in other words, of dyeing in certain colours spots of the cloth, or figures impressed on it, while the ground shall be of a different colour or entirely white, affords another practical application of those principles. A mordant is applied to the part on which the colours are to be impressed; which are by its operation rendered permanent, while from the rest of the cloth they are easily discharged.

The mordant principally used, is the acetate of alumina. It is prepared by dissolving 3 lbs. of alum and 1 lb. of acetate of lead, in 8 lbs. of warm water: the sulphuric acid of the alum combines with the oxide of lead, and the compound being insoluble, is precipitated; the acetic acid remains united with the earth of the alum in solution. There are added 2 ounces of the potash of commerce, and 2 ounces of chalk; the principal use of which seems to be, to neutralize the excess of acid. The superiority of this acetate of alumina as a mordant, to alum, arises from the affinity between its principles being weaker, in consequence of which the alumina more easily unites with the cloth and the colouring matter; and from the acetic acid disengaged, not acting with the same force on the colouring matter as the sulphuric acid would do. The acetate also having little tendency to crystallize, can be more equally mixed and applied. A singular fact with regard to it, to be stated under its history, requires to be attended to in its application as a mordant, that of its being decomposed by heat, part of the alumina being separated, and being re-

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* Annals de Chimie, tom. lxxiv. &c. Retrospect of Discoveries, vol. vii.

dissolved as the liquor cools. It should therefore not be prepared or used warm.

The mordant thus prepared, is thickened with gum or starch ; or with the mucilage prepared from lichens scalded and boiled with a little potash. It is applied by wooden blocks or stamps to the parts of the cloth on which the figures cut in the stamp are designed to be impressed, or by a pencil, if more delicate lines are to be traced. The cloth is afterwards dried thoroughly, is washed in warm water to remove the mucilage and the superfluous mordant, and is then dipt in the dye liquor, usually an infusion of madder; the whole is dyed, but the parts which have been impregnated with the mordant receive a brighter colour than the part which has not : the colour, too, of the former is permanent, while that of the latter is fugitive. It is discharged by boiling with substances having a weak attraction to the colouring matter, principally with bran, and by exposure on the field, repeating these operations alternately. The ground of the cloth is thus rendered white, while the colours of the parts on which the mordant has been impressed, representing the design on the stamp, remain with little alteration.

This mordant, with madder, gives the various shades of red; with weld or quercitron bark, the shades of yellow; and with logwood, a rich but fugitive purple. To diversify the colours, another mordant is likewise employed,—the acetate of iron, prepared by digesting the empyreumatic acid obtained from the decomposition of wood with iron. With madder or logwood it gives black, and by dilution, different shades of purple; with weld, olive, and with quercitron bark, brown. Mixtures of these are also made, which give other colours.

This is the most simple kind of cloth printing. What is more difficult is to have the ground coloured, and figures impressed on it of a different colour. This is done in the following manner. After the cloth has been permanently dyed, by having been impregnated with the mordant, the colour is discharged from certain parts, by stamping these with a weak acid liquor composed of lime-juice, with supersulphate of potash dissolved in it: after being washed, these are again stamped, either with the same or with a different mordant, and dyed with different materials. By combining these methods too, and by dextrously applying to different parts of the cloth different mordants, by stamps adapted to each other, so as to form a regular design, different colours are impressed either on a white or coloured ground; and the design is often rendered more delicate, by the mordant being applied by the pencil where the block cannot easily be applied. The Turkey Red Dye, which is more permanent than others, is discharged by oxymuriatic acid, or, according to a method discovered by Mr Wilson, by oxymuriate of alumina, the only oxymuriate which has the effect *.

The formation of the vegetable pigments, or what are named Lakes, affords another exemplification of the affinities of colouring matter. The colour of certain vegetables is extracted by its proper solvent, generally by water; and there is added to the solution, some substance capable of attracting and combining with the colouring matter, so as to form a precipitate. Thus, if alum be dissolved in an infusion of brazil wood, and an alkaline solution be added, the earth of the alum is precipitated, and combining with the colouring matter, forms a coloured precipitate, or lake. Similar lakes are formed from other coloured vegetables, as from quercitron, turmeric, &c. And the most beautiful of them, carmine, is prepared by a similar process from cochineal, a colouring substance of animal origin. It is not always necessary even that the colouring matter should be in a state of solution. Sir H.

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* Annals of Philosophy, vol. viii. p. 125.

Englefield has shewn, that if the colouring matter of madder be in a state of suspension in boiling water in which alum is dissolved, on adding carbonate of potash the alumina is precipitated, and attracts the colouring matter, forming a rich lake [*]. Sometimes metallic oxides are employed as the basis of such pigments, particularly oxide of tin; muriate of tin being added to the coloured infusion, and being decomposed by an alkali: and Guyton has recommended oxide of tungsten, as affording a basis for lakes superior to any other, in the brightness and permanence of the colour [†].

The vegetable substances used in dyeing are extremely numerous. The colouring matter of the greater number of them, such as all the woods and barks, appears to approach to extract, and admits therefore of few farther observations as to their chemical history. Logwood, the wood of the Hæmatoxylum Campechianum, is of a reddish purple colour, and affords to water very easily its colouring matter: it is used principally for purple dyes, its colour being modified by the different mordants; and it also enters into the composition of the black dyes. Brazil wood, the wood of the Cæsalpina crispa, gives to water a bright red colour, and the colouring matter is easily attracted by alumina and the metallic oxides; the alkalis give it a violet tint, and the acids precipitate it of a fawn-red colour. From experiments on logwood and brazil wood by Chevreul, it appears, that their soluble matter consists principally of colouring matter and tannin, with gallic acid, acetates of ammonia and lime, acetic acid, and a little volatile oil. The same chemist has more lately pointed out the existence of a peculiar crystallizable substance, which is deposited from the watery decoction of logwood, inspissated to a thick consistence; and obtained in larger quantity, by evaporating the liquor to a dry extract, macerating it in alkohol, inspissating this solution, and then adding a little water. This substance is of a rose colour, with considerable lustre; its solution in water is orange-red, and is changed by the stronger acids first to a yellow, and then to a red: sulphurous acid, and sulphuretted hydrogen, destroy the colour. It is soluble in warm water, and separates in crystalline scales by cooling. It is slowly precipitated by gelatin; and in the state in which it exists in logwood with a peculiar extractive matter, is immediately copiously precipitated. Chevreul has named it Hæmatine *.

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[*] Nicholson's Journal, vol. x. p. 215.

[†] Annales de Chimie, tom. xxx. p. 185.

Madder, the root of the Rubia tinctorum, is another red dye, the colouring matter of which is extracted, though rather partially, by water, and of different shades, in repeated macerations, so that at length it gives only a fawn colour; and even after these infusions, it retains much colouring matter, which may be extracted by the action of an alkali. Alum forms in its infusions a brownish red precipitate; and the remaining liquor, when an alkaline carbonate is added to it, gives a blood-red precipitate, which by an excess of alkali is re-dissolved. It is much used both in dyeing and calico-printing, giving numerous shades of red, as it is combined with different mordants. Quercitron is the internal bark of the Quercus nigra: it yields its colour, which is yellow, by infusion to water, and with the common mordants gives a permanent dye. It is much used as a substitute for Weld, the stalks of the Reseda luteola, which were formerly used to furnish a yellow dye, being combined with alum and tartar as mordants, and which also was sometimes combined with madder, to obtain

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* Annales de Chimie, tom. lxvi. lxxxi. or Retrospect of Discoveries, vol. vi. p. 88. viii. p. 145.

orange and other shades. Fustic, the wood of the Morus tinctoria, affords another yellow dye: its decoction in water is of a reddish yellow colour, and it gives a yellow dye to cloth, which, even without the aid of mordants, is permanent; by the use of alum, tartar, and muriate of tin, the colour is rendered brighter. Sumach, the shoots of the Rhus coriaria, is used for giving a fawn colour, which it does when merely boiled in water. With acetate of alumina, it gives a yellow; and as it contains a portion of tannin, it enters sometimes into the composition of the black dyes, and is used as a mordant, to modify other colours, or render them permanent.

Annota is prepared from the seeds of the Bixa orellana, by bruising them, and keeping them in water until they ferment. A colouring matter is formed, of an orange colour, which is dried. It is not perfectly soluble in water, but forms, by infusion or decoction, a liquor of a yellowish red colour, and turbid: the addition of an alkali renders it more soluble, and gives it a bright orange-yellow colour. Acids form with this liquor an orange-coloured precipitate; and a solution of alum forms an orange precipitate still deeper in the colour. Annota is more soluble in alkohol than in water; and hence it sometimes enters into the composition of coloured varnishes. In dyeing it is always mixed with an alkali.

From different species of lichen, is prepared the colouring matter known under the names of Archil and Litmus, so useful to chemists, as the most delicate test of acidity. There is some degree of obscurity with regard to these. Archil is said to be obtained from the Lichen rocella, and Lichen parellus; but other species afford a similar substance. The plant is reduced to powder; a quantity of the potash or soda of commerce is added to it; and it is moistened with urine, and kept moist by successive additions, for some time; it ferments, and gradually acquires a blue or violet colour; it is then dried*. Litmus or Turnsole is the same substance, apparently in a more pure state: it has been said to be prepared from the juice of the Heliotropium tricoceum, or the Croton tinctorium, with which linen rags are impregnated, and which are afterwards reduced into a kind of paste, containing, according to Fourcroy, soda, according to Chaptal, calcareous earth and potash. The latter chemist has remarked, that its colouring matter is of the same nature as Archil. The colouring matter is extracted by water; the infusion is of a purple colour; if it be kept secluded completely from the air, the colour entirely disappears; but it is quickly renewed when the air is admitted. It is also soluble in alkohol, and in this solution exhibits the same phenomenon. It is instantly reddened by the weakest acid liquor; and hence the watery infusion of it, or paper stained with this, affords a very delicate test. The purple tint appears to arise from the operation of a very minute quantity of alkali in the preparation of the litmus, and the effect of an acid is to remove this. Its colour is therefore not much deepened by the alkalis. In dyeing it communicates only fugitive colours, and hence is used only in modifying or heightening others that have more permanence.

SECT. XXXII.—OF AROMA. ACRID PRINCIPLE. BITTER PRINCIPLE. NARCOTIC PRINCIPLE, &c.

I PLACE these principles under one section, and at the close of the history of vegetable substances, as their existence, though maintained by some modern chemists, appears to be doubtful. The sensible qualities from which their names and distinctive characters are derived, are such as may belong to any of the known vegetable principles, and are indeed possessed by those of the most opposite kind; and it is an unphilosophical hypothesis to assume, that there are distinct principles in which they reside. As such principles, however, have been supposed to exist, and as with regard to some of them there are facts which to a certain extent favour the opinion, it may be necessary, in concluding the history of the vegetable substances, to state the observations or the reasonings which have been connected with this subject.

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* Nicholson's Journal, 4to, vol. ii. p. 311.

AROMA. This has been considered as the Principle of Odour in vegetables. The essential oils of plants generally possess their flavour; but many vegetables which smell strongly yield little essential oil; and the oil, when it is obtained, has not that strong odour we should expect, did that of the plant depend on it. This is the case with the violet, jessamine, and many other odoriferous flowers. It was also observed, that if such vegetables be placed in water, and exposed to a gentle heat, not sufficient to volatilize their essential oil, they are deprived of their smell, which is transferred to the water, when the operation is performed in close vessels. The essential oils, too, always lose much of their odour from exposure to the air, though little of the oil itself is dissipated. And, lastly, it has sometimes happened, that the atmosphere around odoriferous plants has not only had their odour diffused through it, but received such an impregnation of inflammable elastic fluid, as to have kindled on the approach of an ignited body. From such facts it was inferred, by some of the older chemists, that there exists in vegetables a principle in which their odour resides; that this is capable of being combined with their other principles, and in particular with their essential oils, to which it communicates the odour of the plant. By Boerhaave it was named Spiritus Rector of vegetables; and in framing the modern nomenclature, it received the denomination of Aroma.

The observations of Fourcroy on this subject * are just. The faculty of exciting the sensation of odour, is a quality which may belong to any kind of matter, and which does belong to many substances, as ammonia, sulphur and its compounds, and many others, in which we cannot suppose the existence of any common principle on which it depends. There is no reason to suppose but that it may exist in vegetable products, without being attached to such a principle in them; and all the facts from which the existence of it has been inferred, admit of explanation, on the supposition that the odour resides in the essential oil, which is sufficiently volatile to be dissipated at a moderate temperature, which may be diffused in atmospheric air, or dissolved by it, and which, suffering chemical changes from exposure to the atmosphere, is deprived of much of its smell. At the same time, the odour may sometimes reside in other proximate principles; and indeed the greater number of these may be distinguished by a smell in general faint, but perceptible.

ACRID PRINCIPLE. The existence of a principle of this kind has been inferred from a few facts with regard to acrid plants. It has been found, that several vegetables are in their recent state extremely acrid to the taste, and display this acrimony in the irritation and inflammation which they occasion when applied to the skin. Such are the roots of the Scilla maritima, Colchicum autumnale, Bryonia alba, and Arum maculatum, and the leaves of the Anemone nemorosa, and of the Clematis erecta. Yet they

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* Annales de Chimie, tom. xxvi. p. 252.

lose this acrimony on being dried, while their other active powers frequently remain. From some of these plants, too, this principle is communicated to water or alkohol by distillation, though no other property but the acrimony is conveyed: in others again, as in squill, according to Vogel, it is not obtained in the distilled water, but is lost by decomposition at the boiling temperature: the acrid principle of this root he farther found to be equally soluble in water and in alkohol *. There appears some reason, from these facts, to admit the conclusion that has been drawn †, that there exists a volatile principle in these plants different from an essential oil, in which their acrimony resides. If its existence shall be considered as probable, however, it has never been obtained so as to be submitted to chemical examination. From some experiments by Einhof on the acrid principle of Horse-radish, it appeared to have the properties of an essential oil, being odorous, volatile, soluble in alkohol, and sparingly soluble in water ‡.

NARCOTIC PRINCIPLE. The existence of such a principle has been inferred from facts similar to those on which that of an acrid principle has been supposed to be established. Many narcotic plants suffer a diminution in their power from age, and are rendered inert by decoction in water. In some cases, the distilled water, as for example that from the leaves of the cherry-laurel, (Prunus lauro-cerasus), has a narcotic power; in other cases it has none.

These facts are inconclusive. The injury which some of these plants sustain from decoction, while, at the same

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* Annales de Chimie, tom. lxxxiii.

† Gren, Principles of Chemistry, vol. i. p. 20. Hermbstaedt, Medical and Physical Journal, vol. i.

‡ Nicholson's Journal, vol. xxvi. p. 111.

time, their powers are not communicated to the water distilled from them, is probably to be ascribed not to the dissipation of a volatile principle, but to changes which its principles suffer, principally to the oxygenation of its extractive matter. And where the narcotic power is communicated to water by distillation, it appears to be proved, that this depends on the presence of the Prussic acid. This acid has been discovered, as has been already stated, (page 302.), in the cherry-laurel, the bitter almond, and other plants possessed of narcotic power: and it has also been found, that the prussic acid, in its pure state, is narcotic. But there is no reason to presume that it exists in other narcotics; and none therefore to infer, that it is the narcotic principle.

Bitter principle. It has been supposed by some chemists, that a principle exists in some of the vegetable bitters, in which their bitterness resides. The properties, however, that have been assigned to it, particularly its equal solubility in water and in alkohol, and its precipitation by certain re-agents, appear to prove, that what has been considered as such is a variety of extract slightly modified, perhaps by intermixture with other principles. Were even its existence established, the name given to it, implying that it is the principle of bitterness, can with no propriety be assigned to it, since many substances possess this quality, in which it has not been proved to exist.

A peculiar substance, artificially formed from certain vegetable and animal products, has been named Bitter Principle. There is no reason, however, to believe that it is naturally formed, or that it exists as a vegetable principle; as a product of the action of nitric acid on indigo, it has been already considered.

Principle in Asparagus. Asparagin. The notice of this I may place under this section, as its nature is not well determined. It was discovered by Robiquet and Vauquelin in the juice of Asparagus. When the expressed recent juice is concentrated by evaporation, crystals are deposited from it, of which some are white and transparent, have a taste rather nauseous, are hard and brittle; the others, though equally white, are not so transparent or hard; they have a saccharine taste, and their crystalline form is different: this Vauquelin regards as a variety of sugar or manna; the other he considers as a new substance; the following are the properties which he has observed to belong to it. It is soluble in water, and its solution gives no indication of acidity or alkalinity; re-agents do not discover in it the presence of any alkaline or earthy base; it is not therefore a neutral salt. It is not soluble in alkohol; nor does it suffer any change from infusion of galls, acetate of lead, oxalate of ammonia, muriate of barytes, or hydro-sulphuret of potash. Nitric acid decomposes it; nitric oxide gas is disengaged, and the liquor assumes a yellow colour and bitter taste, and yields ammonia: it is decomposed by heat, exhales during this decomposition pungent vapours, which irritate the eyes and nostrils, and the smell exhaled is analogous to that from animal substances: it leaves a charcoal, which on incineration gives a very imperceptible trace of earth. From these results, it appears to be a compound of carbon, hydrogen, oxygen, and nitrogen, and, from yielding ammonia, and affording bitter matter when acted on by nitric acid, to be similar in composition to animal substances *.

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* Philosophical Magazine, vol. xxvi. p. 289.

CHAP. III.

OF THE SPONTANEOUS CHEMICAL CHANGES AND DECOMPOSITION OF VEGETABLE SUBSTANCES.

THE changes of composition to which the vegetable principles are liable from the chemical actions of other substances, are in a great measure peculiar with regard to each, as are also the changes they suffer from the application of heat; they have therefore been noticed under their individual history. But, besides these, they are liable to spontaneous changes of composition, at natural temperatures, arising chiefly from the re-action of their constituent elements. These, as being more general, are to be the subjects of consideration under the present chapter.

The term Fermentation has been employed by chemists to denote an extensive series of changes of this kind, in which there is an intestine motion of the parts of the body, and which gives rise to new products; and as this general process varies in its phenomena and results, according to the circumstances under which it happens, or the nature of the vegetable matter subjected to it, three species of it have been distinguished,—the Vinous, the product of which is vinous spirit; the Acetous, which produces acetous acid or vinegar; and the Putrefactive, in which the elements pass off in new combinations in the aërial form. These may be considered under different sections.

SECT. I.—OF THE VINOUS FERMENTATION.

BOERHAAVE appears first to have distinguished fermentation into the three species of vinous, acetous, and putrefactive. He supposed that they succeed each other in an invariable order, that the vinous always precedes the acetous, and that this precedes the putrefactive.

This opinion is so far just, that there are substances which undergo these successive changes. Many weak vinous liquors, by a continuance of the fermentative process, become sour, or form vinegar; and vinegar undergoes decomposition, forms a mould, or passes into a species of putrefaction. But the three kinds of fermentation do not invariably succeed each other. Many vegetable substances become sour, which do not previously assume any vinous state; and a still greater number undergo that decomposition analogous to putrefaction, without having passed through the other stages of fermentation. When they do succeed one another, however, the vinous precedes the others; and it never succeeds them.

The following are the phenomena which occur during the vinous fermentation. The liquor becomes turbid; a kind of intestine agitation takes place; a quantity of aërial fluid is disengaged, which is partly entangled by the liquid, and with its impurities forms a scum on its surface; the quantity of this continues to increase; the volume is augmented; and the temperature is raised a number of degrees. The gas thus disengaged is carbonic acid, and its extrication continues until the end of the process, more or less rapidly, according to the nature of the fermenting liquor, and as it is more or less favoured by circumstances. It appears to be impregnated with part of the principles of the fermenting liquor. Chaptal observed, that water which had imbibed it by being placed in a vessel in the atmosphere above a fermenting liquor, on being kept for a month in open vessels, is converted into vinegar, a flocculent matter being deposited; proving, as he remarked, that the carbonic acid gas had carried with it a little alkohol and extractive matter *.

According to the experiments of Fourcroy and Vauquelin, related in their Memoir on Fermentation †, the carbonic acid gas is frequently mixed with hydrogen, when it is disengaged during the fermentation of the wort of malted barley, without yeast, at a temperature of 80. The wort of the brewers, in fermenting, afforded, however, only carbonic acid; and the hydrogen, therefore, must have been derived from the fecula of the grain.

After a certain time, a few days if the quantity of liquor is considerable, the disengagement of gas and the intestine motion to which this gives rise begin to cease, and the liquor recovers its transparency. If now examined, it is found entirely changed in its qualities; it has lost its bland, or sweet taste, has become pungent, acquired a peculiar odour, and is capable of acting more powerfully on the living system, producing excitement and exhilaration.

This process is independent of any action of the air. It can be carried on in close vessels, when the carbonic acid gas is allowed to escape by a bent tube terminating in water. In this situation, however, the fermentation proceeds, as Chaptal has remarked, more slowly than when the vessels are imperfectly closed, being retarded probably by the pressure of the gas; and hence the necessity, in conducting fermentation on a large scale, of admitting a communication with the atmosphere. Too free an exposure is prejudicial, as it occasions a waste of alkohol and

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* Annales de Chimie, tom. xxxvi. p. 27.

† Annales du Museum National, tom. vii. p. 16. or Translation of the Memoir, Philosophical Magazine, vol. xxv.

aroma *. If the air be excluded, while the gas formed during the fermentation is allowed to escape, Mr Collier has shewn by experiment, that the liquor is stronger than when fermented in open vessels †. This independence, however, of fermentation of the air, is to be understood with some limitation. It holds true with regard to some substances, but not to others. Gay Lussac has remarked, that sugar, with the addition of the yeast of beer, ferments readily, though the air be not admitted. But he found, that the must or juice of the grape does not ferment, if the air has been entirely excluded; and farther, on exciting fermentation in it by the admission of air, the oxygen is consumed, carbonic acid being formed. He inferred from this fact, that the ferment, or principle which excites fermentation in the juice of the grape, is different from yeast, which excites that process in sugar, and that the action of oxygen is necessary to communicate to it that power. In conformity to this he found, that the admission of oxygen is necessary only to the commencement, not to the continuance of the fermentation; and it is singular how small a portion is sufficient to produce the effect. He selected a bottle of grape juice, that had been kept a year in a close vessel, and was perfectly limpid; poured it into another bottle, which was then corked tight, and exposed to the proper temperature for fermentation: in a week fermentation had taken place, and it was soon converted into a vinous liquor. He subjected another bottle of the same juice, which had been kept for a year like the other, but which had not been opened, to the same temperature, and it suffered no change. With gooseberry juice he obtained the same results. When a juice susceptible of fermentation has been exposed to the air, so that it would ferment if left to itself, if it be exposed to the

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* Annales de Chimie, tom. xxxvi. p. 11.

† Manchester Memoirs, vol. v. p. 256.

heat of boiling water in a vessel well closed, it becomes turbid, and a sediment is deposited, and after this it is no longer capable of fermenting, until again exposed to oxygen. And by repeated heating at intervals fermentation may be prevented, even though the air has been admitted each time. Hence the rationale of the process of Appert, of counteracting fermentation and putrefaction in many vegetable and animal substances by heating them to 212°, and completely excluding the air *.

Of the vegetable proximate principles, saccharine matter is that which passes with most facility into the vinous fermentation; and fermented liquors are more or less strong, as the juices from which they have been formed have contained a greater or less proportion of sugar. The sugar in fruits usually exists in that state which forms the uncrystallizable variety, already described, (page 118.), of which grape sugar is an example, and which passes more readily into fermentation than pure sugar, so much so indeed, that it undergoes that process spontaneously. Pure crystallized sugar, however, can also be rendered capable of fermentation with the aid of a ferment; and when added to the juices of the fruits which afford fermented liquors, it gives a more highly vinous product.

Certain circumstances are necessary to cause fermentation to continue and proceed. These are a due degree of dilution in the liquor; a certain temperature; and the presence of substances which favour the subversion of the equilibrium of affinities by which the principles of the saccharine matter would be retained in union, or at least would be prevented from entering into those combinations necessary to form vinous spirit. These substances are named Ferments.

1*st*, A certain proportion of water to the matter susceptible of fermentation is requisite. If the latter is in large quantity proportioned to the water, the fermentation does not commence easily, nor proceed so quickly; on the other hand, too large a proportion of water is injurious, as causing the fermented liquor to pass speedily into the acetous fermentation. The proportions employed by Lavoisier in his experiments on fermentation, were four parts of water to one of saccharine matter.

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* Nicholson's Journal, vol. xxxi. p. 249.

2d, A certain temperature is not less essential. At a temperature lower than 50° of Fahrenheit, fermentation scarcely commences, or, if it has begun, proceeds slowly; and if the temperature be reduced to 32°, it is entirely checked. It proceeds too rapidly when the temperature is much above 55°, and requires to be checked to prevent it from passing into the acetous stage.

Lastly, Certain substances are necessary to excite fermentation. It has been stated, indeed, that sugar alone, dissolved in a certain quantity of water, and placed in a certain temperature, will ferment, but it is doubtful if this happens with a solution of pure sugar; any change which is observed, is imperfect and irregular: nor does the liquor become vinous, but rather sour.

The substance usually added, where an addition is requisite to excite fermentation, is Yeast,—the scum which is collected on the surface, as well as the sediment formed from liquors already in a state of fermentation. This added to a solution of pure sugar, causes it to ferment, and to pass into a vinous liquor. The same substance must be present in the juices of fruits which are capable of spontaneous fermentation, and also in the nutritive grains, as infusions of these, after malting, are capable without yeast of passing, though less rapidly, into fermentation.

What is the nature of the matter which thus excites fermentation, is a question which has often been the subject of investigation, and it is only lately that some light has been thrown upon it.

Lavoisier, in his experiments on fermentation, remarked, that the matter of yeast is a compound of carbon, hydrogen, oxygen, and nitrogen. From the researches of Fabroni, Thenard, and Seguin, it is proved, that it is a substance analogous to gluten or albumen, which is derived from those vegetable juices or infusions that without any addition are capable of fermenting.

Fabroni found, that saccharine matter does not ferment alone, but only by the aid of another substance:—the glutinous or vegeto-animal matter, which exists in the nutritive grains, and which, as he stated, is also contained in the grape, and is deposited from its juice. When the deposition is complete, or rather when the glutinous matter is perfectly separated by repeated filtrations, the juice does not ferment, but the sediment, when mixed with a substance susceptible of fermentation, causes it to pass into this state. The glutinous part of wheat appears, from some of Fabroni's experiments, to be capable of producing, either on the must of the grape deprived of its sediment, or on an artificial mixture, the same effect as the sediment of the must, except that the fermentation is more slowly established, and requires a higher temperature, and the concurrence of tartar; the last, as Berthollet has remarked, probably proving useful from the solubility which its acid communicates to the gluten. He accordingly found, that a mixture of sugar and gluten entered into fermentation, by adding a little tartar to it. It is this vegeto-animal matter, according to Fabroni, which principally constitutes the yeast of wine or beer: and Rouelle long ago found, that the sediment deposited from wines in fermentation is of this nature, as it affords much ammonia when decomposed *.

Thenard had undertaken the investigation of this subject. Since the juices of certain fruits ferment without the

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* { Annales de Chimie, tom. xxxi. p. 299.
{ Chemical Statics, vol. ii. p. 410.

necessity of yeast, he directed his attention to these, to discover the principle they contained, which promotes the fermentation of their saccharine matter. He selected the juice of the gooseberry, which is very susceptible of fermentation. Having pressed it through a linen cloth, it remained turbid, and held in suspension a slight glutinous matter, which was separated by filtration and washed with water. This substance, added to a solution of sugar, caused it to pass into the vinous fermentation. Yet after having produced this effect, it still remained, according to Thenard, insipid, insoluble in water and in alkohol, and no farther altered, except that on being subjected to destructive distillation, it afforded no trace of ammonia. It appears to exist in large quantity in the juice of the gooseberry, in perfect solution; for when the juice had been filtered, on placing it at the proper temperature, it fermented, and during the fermentation lost its transparency, and threw down a sediment. This when examined was found to be glutinous and insipid: thrown on red hot fuel, it burnt like animal matter: distilled, it afforded carbonate of ammonia: added to a solution of sugar, it caused it to ferment rapidly. It appeared therefore to be a substance analogous to the yeast of beer. The same substance he found to be deposited from the juices of the grape, the cherry, apple, pear, and other fruits, during their fermentation, and those which afforded the largest quantity of it were those which run most quickly into the vinous fermentation. It is always deposited, too, as their fermentation proceeds; and a sediment of yeast always appears, according to Thenard, when alkohol is formed.

To this substance he gave the name of Ferment: it is tasteless, does not change the vegetable colours: by drying it loses three-fourths of its weight, from the dissipation of water; thus dried, it is still capable of exciting fermentation, and may be preserved in this state for an indefinite time. It is so little soluble in water, that the water, after standing over it for several hours, on being filtered, exerts no action upon sugar. It is decomposed by diluted nitric acid, is converted into a fatty matter, nitrogen and carbonic acid gases being evolved. Potash acts upon it as it does on animal substances, forms a kind of soap, and causes an evolution of ammonia. In its humid state it is liable to putrefaction, and it affords the products of animal matter when decomposed by heat, the proportion of carbon being large. From 8 parts, Thenard obtained, by destructive distillation, 1.61 of water, 1.31 of oil, and 1.46 of muriate of ammonia on adding muriatic acid. The elastic fluid disengaged, amounting to 0.33, consisted of carbonic acid, and carburetted hydrogen or carbonic oxide, and the residuum amounted to 2.83 of charcoal *.

These researches leave a degree of obscurity with regard to this principle, whether it is a peculiar one, or whether it is merely vegetable gluten, as Fabroni had suggested, and as several of its properties appear to indicate. There appears reason to adopt the latter opinion, more especially as the analysis by Fourcroy and Vauquelin of the nutritive grains † has shewn that gluten is not only contained in wheat, but likewise in barley, a grain very susceptible of fermentation.

Seguin affirmed, that albumen, whether vegetable or animal, is the true ferment. He had discovered it in large quantity in those vegetable juices which pass into the vinous fermentation without yeast: he affirms, that when deprived of it, they became incapable of fermenting, and that having added to saccharine matter this principle, it fermented, and yeast was deposited. He adds, that animal albumen, as the white of an egg, has the same effect. Boerhaave long ago placed this substance among the substances which excite fermentation. According to Fabro-

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* Nicholson's Journal, vol. vii. p. 33.

† Annales du Museum National, tom. vii. p. 1.

ni, however, neither the albumen of the egg, the insoluble part of the animal fibre, nor glue, has the property of exciting fermentation.

Proust has supposed, that the liquid sugar of fruits, and that formed from the nutritive grains by malting fruits, different in its nature, as has already been remarked, (page 119.), from crystallized sugar, is susceptible of fermentation without the presence of any other matter. But this is doubtful. A portion of foreign matter seems always to exist in both these cases, which is deposited as the fermentation proceeds, and is capable of exciting fermentation in a saccharine liquor.

It has been supposed, that no substance enters into the vinous fermentation except sugar. The nutritive grains, indeed, afford fermented liquors; but they are subjected to the previous operation of malting, in which the fecula of the grain is by the process of germination converted into saccharine matter; and this was held indispensible to render them susceptible of fermentation. The practice, however, of the spirit-distillers of this country, proves that this is a mistake. They have been accustomed to add to the malted grain, which they ferment with the view of obtaining a spirituous liquor, a proportion of grain which has not been malted, but merely *mashed*, or ground to powder and infused in warm water; and the proportion of this has been gradually increased, so as to exceed that of malted grain. The infusion from this mixture ferments with yeast, and affords a liquor pungent and spirituous.

The practicability of fermenting from unmalted grain, and the practice itself, though scarcely taken notice of by chemists, appear to have been known in this country for a considerable time. It is mentioned by Dr Irvine in an essay on fermentation, read before a literary society at Glasgow in 1785. He observes, that not only is saccharine matter susceptible of fermentation, but the farinaceous and mucilaginous parts of vegetables have a share in producing this effect. In their pure state, they can neither be changed into wine nor vinegar; but, when mixed with a little sweet matter, they ferment together, and may either change wholly into wine, or wholly into vinegar, according to the proportion of sweet matter mixed with them: if the quantity of sweet matter be great, the farinaceous parts are changed into the same wine with the sweet part: if the quantity of saccharine matter is small, the whole becomes vinegar, and has little appearance of ever having been in the vinous state. Thus, a quantity of meal from wheat, barley, or oats, whose greatest part is farinaceous, when mixed with water, becomes by fermentation a little acid, but seems never to acquire any of the properties of wine. If the same meal be mixed with a quantity of sugar, or any other sweet matter, it falls into the vinous state, and the quantity of spirit produced is much greater than the sweet matter alone would have furnished. He then remarks, that the farinaceous substance of seeds is converted into sweet matter by germination, and that many have supposed, that the powers of vegetation only can produce this change. "Certainly, however," continues he, "the powers of vegetable life are no way concerned, or necessary to it. It is not during the growth only of the seed that this change can be effected; but a quantity of the sweet matter produced by the growth of the seed, mixed with a quantity of the same seed ground into powder, and the whole mixed with the proper quantity of water, will all become sweet, and fall afterwards into vinous fermentation, and be changed into spirits, in the same manner as if the whole had been previously altered by the vegetation of the seed. Were it not for this property of the farina, great loss would frequently be sustained by the farmers in unfavourable seasons; grain that has once begun to grow, and whose vegetation has been stopped, can never be made to grow again. Such grain can never undergo any farther malting: when grain has been made to grow in this improper manner, it can hardly be supposed, that the change into saccharine matter is perfect or complete. It therefore would be less proper for the vinous fermentation, and would furnish a smaller quantity of spirit than grain which had been perfectly malted. This grain, however, when mixed with a quantity of perfect malt, and fermented, furnishes as much spirit as if the whole had been in the state of malt *. The persons in this trade even prefer it to an equal quantity of malt; for in good seasons, when no such half malted or half spoiled grain can be got, they take good grain, reduce it to meal, and mix it with their malt, and are satisfied that they obtain more spirits in this way than from an equal quantity of good malt †."

That fecula alone even, or at least mixed with no more saccharine matter than what is contained in the grain, may be made to ferment, is established by the experiments of Fourcroy and Vauquelin. Six pounds of unmalted bruised barley being treated with alkohol, furnished one ounce two drachms of sugar; the same quantity of malted barley, treated in the same manner, afforded four ounces five drachms. Twenty-four pounds of the flour of the unmalted barley having been put into a vat with seven times its weight of warm water, and four pounds of yeast, entered into strong fermentation, which continued seven days. The liquor at the end of that time submitted to distillation gave a weak spirit, which by rectification afforded alkohol. The quantity amounted to twenty-three ounces. Now Lavoisier had established, that 100 parts of sugar give 58 of alkohol; and as the 24 lbs. of unmalted barley contained only five ounces of sugar, it follows, that four

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* This is doubtful: it is stated from the practice of the spirit distillers, that the product of spirit is rather larger from malted grain, than from a mixture of malt and raw grain.

† Irvine's Chemical Essays, p. 518.

times more alkohol had been formed than that sugar could have furnished; a large quantity of it had therefore been formed from the fecula in the grain. Twenty-four pounds of malted barley bruised having been fermented, under the same circumstances as in the preceding experiment, presented the same phenomena, the proportion of alkohol being three times greater than could have been formed from the sugar in this barley *.

As fecula consists of the same principles as sugar, differing only in the proportions, it is not difficult to admit, that it may be brought into fermentation, and may afford ultimately the same products as saccharine matter, though it is also possible, that the fecula may proceed rapidly through the state of sugar, in passing into the vinous fermentation; and it would appear to do so, if the observation of Dr Irvine be correct, that when the flour of unmalted grain is mixed with a quantity that has been malted, the whole, mixed with water, becomes sweet. According to a late statement by Kirchoff, fecula passes into sugar by the action of the gluten of flour, when they are dissolved in water. He found, that pure starch infused in hot water does not become saccharine; neither does gluten suffer this change when treated in the same way. But if a mixture of starch and gluten be infused in hot water, the starch is converted into sugar: a portion of acid is evolved; the greater part of the gluten apparently remains, but it does not again produce the same change †.

Our knowledge of the series of chemical changes which constitute vinous fermentation, is imperfect. Some essential facts connected with it were established by Lavoisier, but the theory he gave is not altogether just.

The properties of the fermented liquor, its odour, pun-

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* Annales du Museum National, tom. vii.

† Annals of Philosophy, vol. ix. p. 54.

gency, and intoxicating quality, are owing to the presence of a principle, which can be separated from it by distillation, and which, in a pure state, possesses these qualities in a higher degree. It constitutes, in the state of dilution in which it is obtained by distillation, vinous spirit, or, as obtained from different fermented liquors, from which it derives peculiarities of taste and flavour, the spiritous liquors of commerce. These, by certain processes, afford it pure: in this state, it is the Spirit of Wine of the older chemists, the Alkohol of the modern nomenclature.

To ascertain the changes which happen during fermentation, Lavoisier, instead of operating on the sweet vegetable juices, the exact analysis of which is difficult, dissolved a quantity of sugar in water, and caused the solution to ferment, by the addition of yeast. He found reason to conclude, that the water of the fermenting liquid is not decomposed; nor is the presence of the air necessary to the process. Since the only products are the carbonic acid gas which is disengaged, and the alkohol contained in the fermented liquor, it follows that these must be derived from the decomposition of the saccharine matter. In fermentation, therefore, he inferred, that part of the oxygen and carbon of the sugar combine and form carbonic acid; and its hydrogen, with the remaining oxygen and carbon, form the alkohol. "Its effects on sugar are reduced to the mere separation of its elements into two portions; one part is oxygenated at the expence of the other, so as to form carbonic acid, while the other part being disoxygenated in favour of the former, is converted into the combustible substance called Alkohol [*]."

It follows from Lavoisier's experiments, that 100 parts of sugar require about $\frac{1}{72}$ of yeast, deducting the water which is foreign to it; that this produces a little more than

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[*] Elements of Chemistry, p. 196.

35 parts of carbonic acid, and that nearly 58 parts of alkohol are obtained by distillation, about 2 parts of acetic acid and 4 of extract remaining.

Independent of objections which may be made to the details of this theory, from the uncertainty of the composition of the substances concerned, so far as relates to the proportions of their elements; an error was committed by Lavoisier, which affects the general theory, in not attending sufficiently to the operation of the ferment or yeast. This he regarded as serving merely to excite fermentation, and as remaining the same at its termination as at its commencement; but he did not prove this, nor did he explain in what manner it produced this effect.

Fabroni supposed that the ferment operates by its carbon attracting part of the oxygen of the sugar, forming the carbonic acid disengaged; while the remaining sugar partially de-oxidated, enters into combination with its hydrogen and nitrogen, and forms the vinous or fermented liquor, or gives to it at least its pungency and intoxicating quality. Of this theory, however, no proofs are given, in the abstract of Fabroni's opinion by Fourcroy *.

Thenard proposed a view somewhat similar. He mixed a quantity of ferment with five times its weight of sugar, and added water: fermentation commenced, and, in four or five days, the saccharine matter had disappeared, and the liquor, on distillation, afforded diluted alkohol. The residue, after the distillation, was evaporated to dryness, and a substance obtained, nauseous, slightly acid, and feebly attracting moisture. The nature of the acid could not be determined, but, according to Lavoisier, it is the acetous which is obtained in such an experiment. Lastly, of the ferment there remained two-thirds, but this Thenard was surprised to find afforded much less ammonia by distillation than the original ferment. From this fact, which

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* Annales de Chimie, tom. xxxi. p. 299.

appeared to indicate that part of its nitrogen had been abstracted, he concluded, that by mixing it anew with sugar, fermentation would take place, and all the nitrogen would disappear. This accordingly happened: at the end of seven days, the liquor being filtered, a residuum was obtained, which gave no trace of ammonia. It seemed possible, that the nitrogen thus disappearing during fermentation, might be carried off by the carbonic acid gas; but, on collecting this, no nitrogen gas was mixed with it. Since it is not contained either in the gas which escapes, or in the residuum, it must have entered into the composition of the fermented liquor. Yet he could not discover it in the alkohol, the essential product of the fermentation, when he subjected it to various modes of analysis with this view. Still he concluded, that it must exist in it; and the theory which he inferred from these facts is, that all the carbonic acid disengaged does not proceed from the decomposition of the sugar: the first portions of it he assumes are formed from a combination of the carbon of the ferment with the oxygen of the sugar; and the ferment excites fermentation, by producing this change; the equilibrium of affinities between the elements of the sugar being broken, gives rise to their combination, so as to form carbonic acid and alkohol: even a part of the hydrogen of the ferment, he supposes, attracts part of the oxygen of the sugar; and its nitrogen probably enters, with the remaining elements of the sugar, into the composition of the alkohol. The other principles of the ferment not expended in these combinations, form, he supposes, the small quantity of acetic acid, and the insoluble matter which is precipitated. In confirmation of these views, he farther states, that ferment has a strong attraction to oxygen; that it absorbs it from the atmosphere, and forms carbonic and acetic acids, the nitrogen being disengaged *.

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* Nicholson's Journal, vol. vii. p. 40.

Seguin gave a very different view of the theory of fermentation. He supposes, that water is decomposed; that its oxygen unites with the carbon of the ferment, and produces carbonic acid; while its hydrogen combines with the sugar, and converts it into alkohol*. The objection to this theory, as Thenard remarked, is, that more alkohol ought to be obtained than there was sugar; whereas little more than half its weight is produced. And besides, the carbon of the ferment cannot be supposed to furnish all the carbonic acid that is disengaged; nor does alkohol contain so large a portion of oxygen as sugar.

It is obvious, that the facts are not sufficiently ascertained to admit of any certain conclusions, much less of a perfect theory, since, amid the obscurity which still prevails, various suppositions, *a priori*, may be formed as to the reciprocal actions of substances, the elements of which are so much disposed to mutual combinations, as those concerned in fermentation; and the subject must be elucidated by farther research. The general result, however, appears to be, as Lavoisier pointed out, the abstraction of much of the carbon and oxygen of the saccharine matter in the formation of carbonic acid, and hence the predominance of hydrogen in alkohol. Gay Lussac considers fermentation as merely the resolution of sugar, by new combinations of its elements, into alkohol and carbonic acid. Sugar consists of oxygen and hydrogen, in the proportion which forms water, with carbon; the proportions being, as he expresses it, equal volumes of the vapour of water, and vapour of carbon; that is, 3 volumes vapour of carbon, 3 volumes hydrogen, and 1½ oxygen. Alkohol consists of equal volumes of olefiant gas and watery vapour; that is, 2 volumes vapour of carbon, 3 volumes of hydrogen, and ½ volume of oxygen. 1 volume of the vapour of carbon combines with 1 volume of oxygen gas, to form 1 volume of carbonic acid; and there thus remain the 2 volumes of vapour of carbon, 3 volumes of hydrogen, and ½ volume of oxygen, to form alkohol. Reducing these proportions to weight, 100 of sugar will be resolved into 48.66 of carbonic acid, and 51.34 of alkohol *.

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* Nicholson's Journal, vol. vii. p. 45.

By the process of fermentation, liquors are formed possessed of an intoxicating quality, but differing from each other in their vinous strength, their taste, flavour, and other qualities,—differences owing partly to the circumstances under which the fermentation has been conducted, but more to the substances from which they have been formed. They may be arranged under two divisions,—what are named Wines, formed by fermentation from the sweet juices of fruits, and the various kinds of Ale or Beer, formed from the nutritive grains, previously subjected to the process of germination or malting.

The juice of the grape affords a wine much superior to any other. It is highly saccharine, without much acid, or matter liable to afford acid; its flavour is agreeable, and it contains the principle necessary to excite fermentation. Hence it passes readily into that state, and affords a rich vinous liquor. Numerous varieties of wines are formed from the grape, modified by climate, soil, and culture, in consequence of which it is more or less saccharine, and intermixed with other principles from which it derives flavour and other qualities. The product is not less influenced by the manner in which the fermentation is conducted; whether it has been rapid or slow, whether the air has been freely admitted, and the gas allowed to escape freely, or the reverse; or whether it has been checked before it has been completed. Hence the distinction of sweet wines, or those containing a portion of saccharine matter; of strong and spirituous wines, in which a rich juice has

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* Annales de Chimie, tom. xcv. Annals of Philosophy, vol. vii. p. 598.

been completely fermented, so as to furnish a large proportion of alkohol; of sparkling wines, in which a quantity of carbonic acid is retained by the manner in which the fermentation has been conducted; and rough or astringent wines, in which some astringent matter originally contained in the fruit is retained. Wines too differ greatly in their flavour, which is derived from the grape, and in the different wines is varied by the mixture of different varieties of grapes. The colour of wines is derived, not from the juice, but from the external pellicle of the fruit: hence colourless wines are prepared from the red grape, by expressing the juice carefully, and allowing none of the husks to remain mixed with it; while, by an opposite practice, or by macerating the juice, while fermenting, on the husks, colour is communicated. All wines contain a portion of super-tartrate of potash derived from the juice; this they deposite slowly, in the gradual fermentation they suffer in the cask; and to this, as well as to other changes produced by this slow fermentation, is owing the improvement of wine from age.

Wines are formed from other fruits, as from the currant, apple, pear, &c. The juices of the currant, gooseberry, &c. contain too large a proportion of acid, and too little saccharine matter, to furnish wine equal to that from the grape, but are improved by adding sugar to the juice, before fermentation. The great deficiency in these vinous liquors, independent of their flavour being inferior to that of the grape, is the redundance of acid, which is only imperfectly concealed by the addition of sugar. This is owing, as Dr Macculloch has remarked, to the acid contained in these fruits being principally the malic, while in the grape it is the tartaric, in the state of super-tartrate of potash. The former remains soluble, and it does not appear to suffer decomposition in the fermentation; the latter, there is some reason to believe, is in part decomposed, and at least much of it is deposited in the state of super-tartrate of potash, as the fermentation proceeds, from its inferior solubility in the vinous liquor. Some advantage appears to be derived from adding tartar to the juices of these fruits, in fermenting them. Various methods have been employed to improve these wines, of which the principal are adding sugar, and a portion of brandy. The former, however, serves merely to conceal the acid; the latter has been supposed to obviate acescency, but, from Dr Macculloch's observations, it appears to have no such effect; and to whatever wine it is added, whether that of the grape or other fruits, it proves injurious to the taste and flavour, and to the effects on the stomach and system. Cyder, from the juice of the apple, and perry from that of the pear, retain a large quantity of carbonic acid, which communicates pungency and a sparkling quality. There also remains in these liquors extractive matter or mucilage, which renders them liable to pass into the acetous fermentation.

The other fermented liquors, are those from barley and other grains, forming the different varieties of ale and beer. In the preparation of these, the grain is steeped in water for 50 or 60 hours, by which the husk is softened, and a portion is imbibed by its substance. The water is run off, and the moistened grain is spread on the floor of a chamber, to the depth of 10 or 12 inches: and sometimes to accelerate the process or carry it farther, it is sprinkled with water; the light too is in a great measure excluded. It begins to germinate, absorbs oxygen, and gives out carbonic acid: in consequence of this chemical action the temperature rises; and to prevent it from rising too high, as well as to render the process as uniform as possible through the whole grain, it is turned up, and is gradually spread into a thinner heap. The germ, in the course of this operation, unfolds, the fibres of the radicle shoot out, and the plumula gradually elongates, forming what the brewers call the Acrospire. The progress of the process is known by the extent of this elongation, which is permitted to go on for a longer or shorter time according to the quality of the grain, and the kind of fermented liquor that is to be formed; if it is not sufficiently advanced, the liquor, it is supposed, is liable to become acescent; if it is allowed to advance too far, much of the saccharine matter is consumed. But considerable difference of opinion has prevailed as to the period at which it ought to be checked: the malted grain is stated to be of best quality when the acrospire proceeds two-thirds through the grain, though it has been the practice to carry on the process until it is farther advanced. When it is to be checked, the grain is dried by the heat of a kiln, which is raised gradually, and which for different purposes is raised to different degrees.

The grain, after having been malted, is freed from the small projecting shoots, and is ground to coarse powder in a mill, or crushed between rollers. This is infused in warm water in the mashing tun: the temperature at which this is to be used is of importance, since, if not sufficiently high, the saccharine matter is not properly extracted, while if too high, the farina becomes pulpy; the temperature at which the water is generally used for the first infusion, is between 160° and 170°. This, after a few hours maceration, is drawn off, and a fresh quantity added. These liquids form the wort: this, previous to its fermentation, is boiled with some bitter vegetable, generally hops, but frequently also other bitter herbs; the advantage of which, besides the flavour and taste which it communicates, is to check the tendency of the liquor to acescency. When the temperature has subsided, a portion of yeast is added, by which fermentation is sooner excited; this, after it has continued a certain time, is checked before it is complete, and the liquor is drawn off. In this manner are formed the different kinds of beer, ale, and porter; the process being varied with regard to each of these, and different additions being made besides the malted grain. They are weaker than wines, and from this, as well as from the portion of mucilaginous and extractive matter which they contain, are more liable to become acescent; but they are possessed of the same general qualities, agree in the effects they produce on the animal system, and afford a portion of alkohol by distillation. Their narcotic power is often increased by the addition of certain substances, and is greater, therefore, than is proportioned to their strength as vinous liquors: and it is somewhat modified by the bitter matter which the stronger kinds of them contain.

The process of malting is obviously nothing more than germination artificially excited, with the view of converting the fecula into saccharine matter, the theory of which has been already considered, (page 35.). It appears, however, that the whole fecula does not suffer this change; a portion of it still remains in the grain, which may even be extracted from it pure; and which, Dobereiner, in his researches on this subject, has remarked *, is white, brilliant, and possessed of the physical characters of starch from the natural grains. Its chemical properties, however, are somewhat different. It is soluble in water at a temperature from 150 to 160 of Fahrenheit, while natural starch requires for its solution a temperature from 185 to 195. The solution of the former, with the addition of yeast, scarcely ferments, or suffers much change at a temperature from 75° to 85°, but if a little sugar is added to it, it soon passes into a strong fermentation; the watery solution of the latter readily ferments, when it is mixed with yeast, at a temperature of 75°. When the fecula, however, of the malted grain is extracted by infusion, along with the sugar and gluten which the grain also contains, it suffers some modification from these, as it forms a solution which is liquid, and which does not become ge-

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* Annales de Chimie, tom. xc. p. 29.

latinous. It also undergoes some change in the subsequent operation of the drying and torrefaction of the malted grain; fecula by roasting, it has been already stated, is rendered more soluble in cold water, and this appears to be the case also in the fecula of malted grain. Doberciner accordingly states, that a portion of starch is always to be found dissolved in malt liquors, which probably adds to their nutritive quality. It is this also in part which renders them liable to acidity.

The saccharine product formed by the changes which the fecula suffers in malting, it has already been remarked, (page 98.), is not pure sugar; it is inferior in sweetness, and cannot be rendered concrete, but forms by evaporation of its solution a viscid mass. It is therefore analogous to the sugar of the grape.

From fermented liquors, spirituous liquors are obtained by distillation. Brandy, the purest of these, is obtained by distillation from wine: Rum, from the fermented juice of the sugar cane: and from the different grains, what is named Malt Spirit is formed. In this country, to prepare the last of these, the liquor fermented from the mixture of malted and unmalted grain is subjected to distillation, and the product is rendered stronger and purer by distilling it a second time. The peculiar flavour of these spirituous liquors, depends probably on a small portion of essential oil, derived from the vegetable matter from which they have been prepared, and not altogether changed by the fermentation. Scheele remarked, that when the spirit from malted grain is exposed to intense cold, a white sediment is deposited, which when heated melts like oil, and added to pure brandy gives it the unpleasant flavour of recent malt spirit. Koerte and Gehlen have made some experiments on this substance. They found it in the first distilled product of the wash from fermented grain in abundance, rendering it milky, and gradually separating on the surface. Its taste and flavour are nauseous. It evaporates in the atmosphere, gives a greasy stain to paper, is soluble in alkohol, but not in water. They consider it as a product of the fermentation of grain *.

The art of obtaining, by distillation, spirituous from fermented liquors, was unknown to the ancients. It is supposed to have been discovered by the Arabians, and was practised during the dark ages. The method of rectifying these, so as to obtain Alkohol, was known to some of the earlier alchemists.

It was generally supposed, that the alkohol produced by distillation from fermented liquors pre-exists in them, and is merely separated by the heat; a conclusion founded on the similarity in the action of wine and of alkohol on the living system, and on the consideration of the very moderate heat required to draw off the spirit, not sufficient apparently to produce any new combination. Fabroni maintained the opinion, which had been before suggested, that the spirit is formed from the principles of the fermented liquor during the distillation; and supported this by the result of experiments, in which alkohol added to wine could be recovered from it, but no additional portion procured. The experiment by which this is established, is to take fresh wine with which one-hundredth part of alkohol has been mixed, and to add to this as much potash as is found by a previous experiment to be necessary to precipitate the resinous colouring residue. It is then strained and put into a glass tube graduated into 100 equal parts, and as much potash is added as it can dissolve. The hundredth of alkohol which had been added, will rise, and swim on the surface of the alkaline solution, of the same degree of strength that had been added, if the experiment is performed sufficiently quickly to lose nothing by evaporation. " Now, if by this means," says Fabroni, " I procure only the same quantity of alkohol from the wine that

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* Annales de Chimie, tom. lxxxi.

I knew it contained before, and no more, it appears to me, that I have a right to conclude, that that which I obtain from the same wine by distillation, did not exist in it before, but that it is the operation of distillation which forms it." He adds, that by the same method he could not discover in new wine any alkohol, though he could obtain from it 20 or 25 parts of brandy in 100 by distillation *.

Admitting the accuracy of these facts, the conclusion does not follow; for the alkohol formed during the fermentation may be in more intimate combination with the principles of the wine, than a portion of alkohol newly added and immediately operated on will be. But Mr Brande, in repeating these experiments, did not obtain the same results. He found, that the other ingredients of the wine prevented the separation of the spirit from it by the action of an alkali; and when alkohol was added to wine in proportions much larger than that stated by Fabroni, no portion of it was obtained by the addition of sub-carbonate of potash; it was only when so large a proportion as one to three was employed, that there was any separation, and even then it was very imperfect. It is evident, therefore, that supposing alkohol to pre-exist in wine, it cannot be expected to be obtained in this mode. Mr Brande afterwards discovered a method by which it is detected. He found, that by the addition of acetate or sub-acetate of lead to wine, a dense insoluble precipitate is formed, consisting of a combination of the metallic oxide with the acid and the colouring extractive matter of the wine, and a colourless fluid remains, containing alkohol, water, and the acid of the metallic salt. On adding to this, sub-carbonate of potash, the alkohol can be procured, and this even in as large a quantity as can be obtained by distilla-

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* { Annales de Chimie, tom. xxxi. p. 303.
{ Nicholson's Journal, 4to, vol. iv. p. 46.

tion *. Thus to eight measures of port wine, one part, by measure of a concentrated solution of sub-acetate of lead, was added: the filtered liquor was colourless, and afforded alkohol on the addition of sub-carbonate of potash; the quantity being 22.5 from 100 measures of the wine. The same wine yielded by distillation 22.3 of alkohol from 100 measures. Similar results were obtained from other wines. Hence it is evident, "that no alkohol is *formed* during the distillation of wines, and that the whole quantity found after distillation, pre-existed in the fermented liquor." The same conclusion was drawn about the same time by Gay Lussac, from a similar experiment;—shaking wine with levigated litharge, so as to abstract the colouring and extractive matter, and then adding sub-carbonate of potash; and also from the fact which he established, that alkohol is volatilized from wine in a vacuum at 60° of Fahrenheit †. Mr Donovan had also shewn, that it is volatilized, at a temperature not higher than 56, from the liquor fermented from malt, placed *in vacuo*, and aided by cold applied to the receiver.

The quantity of alkohol, however, afforded by wines, (with regard to which Mr Brande gave a number of results from experiments), is greater than what would be inferred from their vinous strength; port wine, for example, yielding 22 per cent. of alkohol, of the specific gravity of 0.825, while brandy yields not much more than twice this quantity, or 53 per cent. It appears, therefore, that the spirituous strength and pungency of the alkohol in wine is modified by the ingredients combined with it, and perhaps by the permanence of the combination. Mr Brande found, that distilled port wine tastes stronger, and is more heating, than the wine in its original state, and that these qualities are impaired, and the wine reduced nearly to its original flavour, by the addition of its acid and extractive matter *. The following table, founded on Mr Brande's experiments, shews the proportions of alkohol afforded by distillation from the principal wines, and from other fermented and spirituous liquors.

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* Mr Brande found by previous experiment, that from mixtures of alkohol and water, the alkohol, when it exceeded the proportion of 16 per cent. could be obtained within 0.5 per cent. by the action of sub-carbonate of potash.

† Annales de Chimie, tom. lxxxvi. p. 176.

Wine.	Proportion of Alkohol, per cent. by measure.	Wine.	Proportion of Alkohol, per cent. by measure.
Port	21.40	Red Hermitage	12.32
Ditto	22.30	Hock	14.37
Madeira	19.34	Ditto	8.88
Ditto	24.42	Vin de Grave	12.80
Sherry	18.25	Frontignac	12.79
Ditto	19.83	Cote Roti	12.32
Claret	12.91	Constantia	19.75
Ditto	16.32	Tent	13.30
Calcavella	18 10	Tokay	9.88
Lisbon	18.94	Raisin Wine	25.77
Malaga	17.26	Grape Wine	18.11
Red Madeira	18.40	Currant Wine	20.55
Malmsey Madeira	16.40	Gooseberry Wine	11.84
Marsala	25.87	Cyder	9.87
Ditto	17.26	Perry	9.87
Red Champagne	11.30	Porter	6.80
White Champagne	12.80	Ale	8.88
Burgundy	14.53	Brandy	53.39
Ditto	11.95	Rum	53.68
White Hermitage	17.43	Hollands	51.60

Chaptal, in his analysis of wines, found †, that the alkohol they afford varied much in quantity; some rich wines furnished a third of spirit, while some weak wines did not give more than a fifteenth. He found a portion of acid always present,—all wines reddening test paper: it appeared to be the malic acid, with a small portion of the

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* Philosophical Transactions, 1811, 1815.

† Philosophical Magazine, vol. xi. p. 123. 565.

citric: it is contained in larger quantity in the wines from other fruits, as cyder; and predominates in the fermented liquors from grain. He supposes, with some probability, that it is the cause of the disagreeable flavour the spirit distilled from them has, compared with that distilled from wine: this spirit, at its first distillation, he found always acidulous. The richer wine is in spirit, the less malic acid does it contain; and hence the richest wines, under the same mode of distillation, furnish the most agreeable and purest spirit. Wines also always contain a portion of tartar, derived from the grape, and which they slowly deposite. They hold dissolved too, a quantity of extractive matter, derived from the same source, and which is more abundant in new than in old wines. To these principles is to be added, the colouring matter derived from the pellicle of the grape, and dissolved by the alkohol, as the fermentation proceeds. This is often slowly deposited, and may at once be precipitated by adding lime, which combines with the malic acid, and attracts the colouring matter. This precipitate is insoluble in water, either cold or warm, and alkohol has scarcely any effect on it. Lastly, there is the aroma of wine, or principle which gives it its peculiar flavour, and which is so delicate as to be destroyed by heat.

From the spirituous liquors of commerce, Alkohol may be obtained; and having considered the production of this principle, it remains to state its properties in its pure state.

The process for obtaining it, varies according to the kind of spirituous liquor from which it is extracted. The purer kinds, as brandy, afford it by repeated distillations, a portion of the water remaining at each distillation in the retort; the alkohol passes over less and less diluted, and may at length be obtained pure, or at least can be obtained in such a state by adding, in the latter distillations, a little potash to abstract the water more completely. When it is to be obtained from malt spirit, the process is more complicated.

The spirit is first distilled, to free it from the greater part of the water mixed with it, and the oily or extractive matter derived from the grain. There is added to the distilled spirit sub-carbonate of potash, in the proportion of an ounce to a pint; the sub-carbonate having been dried perfectly, and added warm. It attracts much of the water, and forming a solution of greater specific gravity than the purer spirit, subsides to the bottom. The spirit is poured off, and is distilled from a little of the carbonate, (about half the quantity before employed), with a gentle heat, stopping the distillation before it come to dryness.

The spirit thus obtained, though strong, has a disagreeable flavour, derived from the alkali. To free it from this, and obtain it more pure, it is subjected to another distillation, with the addition of a small quantity of alum, about one drachm to the pint; a little recently prepared charcoal powder is also frequently added, to remove more completely any unpleasant flavour. Some have supposed, that alkohol thus distilled from saline substances suffers some change, besides mere concentration, from their action *; but Th. Saussure found, that in properties and composition it is the same as alkohol rectified without such additions.

Alkohol obtained by these processes, is of a specific gravity of about 0.835; but it may be more highly rectified, by repeated distillations from substances having a strong affinity to water. With pure potash it may be brought to the specific gravity of 0.815; and Dr Fordyce furnished a quantity used in the first experiments of Gilpin, at .813. By using muriate of lime, as proposed by Lowitz and Richter, it may be obtained still lighter. Dr Black brought it to 800: in the tables of Chaussier, it is stated at the temperature of 60° at .798; and Lowitz succeeded in obtain-

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* Annales de Chimie, tom. lxxxvi. p. 314.

ing it at the temperature of 68° at .791. This is the lowest specific gravity at which it has been procured, and therefore the purest alkohol, though it is uncertain if even at this strength it is free from water; nor have we any method of determining when it is so.

The strength of alkohol is best judged of from its specific gravity. It combines with water in every proportion, and this is always accompanied with an increase of density, which is different in the different proportions. Hence the specific gravities of such mixtures cannot be inferred *a priori*, but must be determined by experiment. This is a subject of much importance, from its relation to the strength of the spirituous liquors of commerce; and has hence often engaged the attention of chemists. The labours of Blagden and Gilpin have been extensive with regard to it, and the results they have established are perhaps the most accurate. In their first report, published in the Philosophical Transactions for 1790, the specific gravities, from standard alkohol, through the several mixtures of it with water in different proportions, down to equal parts, were given. In a supplementary report in the Transactions for 1792, the specific gravities of the mixtures in which the proportions of water are larger were added. And in the volume for 1794, a set of tables were published, shewing the specific gravity of every mixture of alkohol and water, from 100 of alkohol to 1 of water, and 100 of water to 1 of alkohol, at the various temperatures from 30° to 80°. I insert an abridged table from these, shewing the specific gravities of the different mixtures, for every 5° of temperature between 30° and 80°. Alkohol of the specific gravity of .825 at 60°, was selected as the standard, as being obtained easily, and as it is uncertain what constitutes real alkohol, or to how low a degree of specific gravity it might be brought. Alkohol of this specific gravity consists, according to Gilpin, of 100 of alkohol of the specific gravity of .814, and 4.5 of water.

Heat.	The pure spirit.	100 spirit to 5 water.	100 spirit to 10 water.	100 spirit to 15 water.	100 spirit to 20 water.	100 spirit to 25 water.	100 spirit to 30 water.
30°	.83896	.84995	.85957	.86825	.87585	.88282	.88921
35	83672	84769	85729	86587	87357	88059	88701
40	83445	84539	85507	86361	87134	87838	88481
45	83214	84310	85277	86131	86905	87613	88255
50	82977	84076	85042	85902	86676	87384	88030
55	82736	83834	84802	85664	86441	87150	87796
60	82500	83599	84568	85430	86208	86918	87569
65	82262	83362	84334	85193	85976	86686	87337
70	82023	83124	84092	84951	85736	86451	87105
75	81780	82878	83851	84710	85496	86212	86864
80	81530	82631	83603	84467	85248	85966	86622

Heat.	100 spirit to 35 water.	100 spirit to 40 water.	100 spirit to 45 water.	100 spirit to 50 water.	100 spirit to 55 water.	100 spirit to 60 water.	100 spirit to 65 water.
30°	.89511	.90054	.90558	.91023	.91449	.91847	.92217
35	89294	89839	90345	90811	91241	91640	92009
40	89073	89617	90127	90596	91026	91428	91799
45	88849	89396	89909	90380	90812	91211	91584
50	88626	89174	89684	90160	90506	90997	91370
55	88393	88945	89458	89933	90367	90768	91144
60	88169	88720	89232	89707	90144	90549	90927
65	87938	88490	89006	89479	89920	90328	90707
70	87705	88254	88773	89252	89695	90104	90484
75	87466	88018	88538	89018	89464	89872	90252
80	87228	87776	88301	88781	89225	89639	90021

Heat.	100 spirit to 70 water.	100 spirit to 75 water.	100 spirit to 80 water.	100 spirit to 85 water.	100 spirit to 90 water.	100 spirit to 95 water.	100 spirit to 100 water.
30°	.92563	.92889	.93191	.93474	.93741	.93991	.94222
35	92355	92680	92986	93274	93541	93790	94025
40	92151	92476	92783	93072	93341	93592	93827
45	91937	92264	92570	92859	93131	93382	93621
50	91723	92051	92358	92647	92919	93177	93419
55	91502	91837	92145	92436	92707	92963	93208
60	91287	91622	91933	92225	92499	92758	93002
65	91066	91400	91715	92010	92283	92546	92794
70	90847	91181	91493	91793	92069	92333	92580
75	90617	90952	91270	91569	91849	92111	92364
80	90385	90723	91046	91340	91622	91891	92142

Heat.	95 spirit to 100 water.	90 spirit to 100 water.	85 spirit to 100 water.	80 spirit to 100 water.	75 spirit to 100 water.	70 spirit to 100 water.	65 spirit to 100 water.
30°	.94447	.94675	.94920	.95173	.95429	.95681	.95944
35	94249	94484	94734	94988	95246	95502	95772
40	94058	94295	94547	94802	95060	95328	95602
45	93860	94096	94348	94605	94871	95143	95423
50	93658	93897	94149	94414	94683	94958	65243
55	93452	93696	93948	94213	94486	94767	95057
60	93247	93493	93749	94018	94296	94579	94867
65	93040	93285	93546	93822	94099	94388	94689
70	92828	93076	93337	93616	93898	94193	94500
75	92613	92865	93132	93413	93695	93989	94301
80	92393	92647	92916	93201	93488	93785	94102

Heat.	60 spirit to 100 water.	55 spirit to 100 water.	50 spirit to 100 water.	45 spirit to 100 water.	40 spirit to 100 water.	35 spirit to 100 water.	30 spirit to 100 water.
30°	96209	.96470	.96179	.96967	.97200	.97418	.97635
35	96048	96315	96579	96840	97086	97319	97556
40	95879	96159	96434	96706	96967	97220	97472
45	95705	95993	96280	96563	96840	97110	97384
50	95534	95831	96126	96420	96708	96995	97284
55	95357	95662	95966	96272	96575	96877	97181
66	95181	95493	95804	96122	96437	96752	97074
65	95000	95318	95635	95962	96288	96620	96959
70	94813	95139	95469	95802	96143	96484	96836
75	94623	94957	95292	95638	95987	96344	96708
80	94431	94768	95111	95467	95826	96192	96568

Heat.	25 spirit to 100 water.	20 spirit to 100 water.	15 spirit to 100 water.	10 spirit to 100 water.	5 spirit to 100 water.
30°	.97860	.98108	.98412	.98804	.99334
35	97801	98076	98397	98804	99344
40	97737	98033	98373	98795	99345
45	97666	97980	98338	98774	99338
50	97589	97920	98293	98745	99316
55	97500	97847	98239	98702	99284
60	97410	97771	98176	98654	99244
65	97309	97688	98106	98594	99194
70	97203	97596	98028	98527	99134
75	97086	97495	97943	98454	99066
80	96963	97385	97845	98367	98991

The specific gravity of the mixtures of alkohol and water is best discovered by the hydrometer or gravimeter, of which there are different kinds in use. That of Fahrenheit, improved by Nicholson and Guyton[*], is the most accurate and delicate.

Alkohol is colourless and transparent. Its odour is fragrant, and its taste hot and pungent. It acts powerfully on the animal system, exciting exhilaration and intoxication.

It is always fluid, not congealing at degrees of cold at which all other liquids congeal. Its congelation was said to have been effected by Mr Hutton, at a temperature estimated to be below —110°[†]; but the method of making the experiment was not made public, and it has not been established by any subsequent result.

Alkohol is highly expansible, and is also very volatile. It evaporates quickly, when exposed to the atmosphere: it distils in close vessels slowly at 100°, and boils at 165°. The specific gravity of its vapour is, according to Gay Lussac, 1.613. If suddenly exposed to a high temperature, it is decomposed. When transmitted through an ignited tube, it is converted into one of the varieties of oxycarburetted hydrogen gas: watery vapour and carbonic acid gas are at the same time formed; charcoal is deposited, which by incineration affords traces of potash, silex, and lime; and a kind of crystallized volatile oil was observed by Vauquelin to be formed in the process, which Saussure has likewise observed.

Alkohol is highly inflammable. It kindles when the temperature is not much above 300°, and burns with a blue lambent flame, without any sensible smoke, and, when pure, without residuum. The products of its combustion are water and carbonic acid gas. The quantity of water was found by Lavoisier to amount to about eighteen from sixteen parts.

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[*] Nicholson's Journal, 4to, vol. i.

[‡] Ibid. 8vo, vol. xxxiv. p. 166.

By performing the combustion in vessels adapted to collect the products, he endeavoured to infer from these the composition of alkohol *. Of a quantity kindled in a lamp, there were burnt 93.5 grains, and, in the combustion of this, 110.32 grains of oxygen were consumed: there was produced carbonic acid gas to the amount of 95.28 grains; and a quantity of water was condensed, calculated to amount to 108.54 grains. On these grounds he concluded, that alkohol consists of 28.5 of carbon, 7.8 of hydrogen, and 63.5 of water. But allowing the accuracy of the results, which Lavoisier himself considered only as approximations, it is obvious, that the inference, that the large quantity of water obtained in the combustion above that which could have been derived from the quantity of oxygen consumed, pre-existed in the alkohol, does not follow, since it may be rather the elements of this water; or, in other words, the alkohol may contain a portion of oxygen, which would contribute, with the oxygen gas consumed, to the formation of the water and carbonic acid.

To determine the composition of alkohol, T. Saussure employed the different methods of burning a given weight of it in oxygen gas mixed with a certain proportion of atmospheric air, observing the quantity of oxygen consumed, and of carbonic acid and water formed; of detonating the vapour of alkohol with oxygen gas in a tube; and of decomposing it by passing it through an ignited porcelain tube. The two latter modes he regarded as more accurate than the first. The results of the one gave as the elements of alkohol, of the specific gravity of 0.792, at 68° of Fahrenheit, carbon 48.82, hydrogen 15.82, oxygen 41.36; those of the other, carbon 43.65, oxygen 37.85, hydro-

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* Memoires de l'Acad. des Sciences, 1784, p. 598.

gen 14.94, nitrogen 3.52, ashes 0.04 *. These he regarded, however, only as approximations. He has since resumed the investigation, employing the last of these methods as the least complicated, and susceptible of the greatest precision. The alkohol on which he operated was of the specific gravity 0.830 at 63°; a liquid composed, according to the table of Richter on the condensation of mixtures of alkohol and water, of 13.8 water, and 86.2 absolute alkohol; but he reduces the results of the analysis by calculation to this absolute alkohol, excluding of course the oxygen and hydrogen of the contained water. The products of the decomposition were oxycarburetted hydrogen gas and water, with minute portions of an oily matter, and charcoal. This gas required for its combustion oxygen in the proportion of three measures to two of the carbonic acid gas formed; this is exactly the quantity which olefiant gas requires; hence, as it afforded also in its combustion a portion of water, its composition is such that it is represented by olefiant gas and water; the proportions, according to Saussure, are 100 of the former, and 47.6 of the latter. But alkohol itself yields this gas and water in its analysis, (the other products being so minute that they may be neglected), hence alkohol also is represented by olefiant gas and water; the proportions which Saussure assigns are 61.13 of the former, and 38.87 of the latter, or 100 and 63.58; that is, of the elements of these in these proportions: and substituting these elements, it follows, that 100 parts of the absolute alkohol of Richter are composed of carbon 51.98, oxygen 34.32, hydrogen 13.70. What proportion of the oxygen and hydrogen exists in the state of water remains uncertain. Saussure supposes the most probable conjecture to be, that alkohol contains a quantity of elementary water double in weight to that

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* Nicholson's Journal, vol. xxi. p. 222.

which exists in ether; according to this, pure alkohol would be represented by 100 of olefiant gas and 50 of water, as is nearly the case with the gas obtained by passing aqueous alkohol through a red hot tube; 100 parts of Richter's absolute alkohol would contain 91.7 of pure alkohol, and 8.3 of water: and 100 parts of pure alkohol would be composed of carbon 56.68, oxygen 29.44, hydrogen 13.88*. Gay Lussac has calculated, from the preceding results, that alkohol consists of equal volumes of olefiant gas and aqueous vapour; for being composed, according to Saussure, of 100 of olefiant gas by weight, and 63.58 of water, if these are reduced to volume, on the *data* that the density of olefiant gas is 0.978, and the density of watery vapour 0.625, they give the proportions of 102.5 of the gas, and 101.7 of the vapour, which may be regarded as approximations as near as can be expected to equal volumes. The density of the vapour of alkohol Gay Lussac finds to be 1.613, from which it follows, that the condensation in the combination is one half of the volume of the two elastic fluids †.

Alkohol combines with water in every proportion. Though, in this case, no new properties are acquired, yet it is a real chemical combination, as is evident from the condensation which accompanies it. The specific gravity of the compound is always greater than the mean of the specific gravities of the separate fluids. Thus, if one part of alkohol, whose specific gravity is 817, be mixed with one of water whose specific gravity is 1000, the specific gravity of the compound will not be the mean 908.5, but will be not less than 934; and a difference will obtain in whatever proportions the fluids are mixed. This difference proceeds in a decreasing ratio; that is to say, when ten parts of alkohol are mixed with one of water, the difference in the specific gravity produced is greater than when the ten parts are mixed with two, and greater in this, than when mixed with three. The progression, however, is not regular; and hence, the specific gravity of any possible mixture of alkohol and water cannot be calculated *a priori*, but must be determined by experiment.

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* Journal de Physique, tom. lxxviii. p. 115. Annals of Philosophy, vol. iv. p. 35. Alkohol contains no nitrogen. Its presence, in Saussure's first experiments, had arisen from its having been given out by the water over which the oxycarburetted hydrogen had stood.

† Annales de Chimie, tom. xcv. p. 311.

The greater density which the combination of alkohol with water acquires, is accompanied with a diminution in the capacity for heat; hence, a rise of temperature accompanies their union. It is also accompanied with a hissing noise, and the formation of air bubbles. Alkohol diluted with an equal weight of water, forms what is named Proof Spirit.

From its affinity to water, alkohol precipitates many neutral salts from their aqueous solutions. There are others which it does not precipitate, and which, even in its pure state, it is capable of dissolving, particularly those which are deliquescent, which have ammonia, lime, or magnesia for their base; or the nitric or muriatic acid for their acid. Many of these salts give a peculiar colour to the flame of alkohol in burning.

From its solvent power with regard to salts, alkohol is a useful re-agent in the analysis of mineral waters. The table of their degrees of solubility in it has been already given.

Alkohol combines with the alkalis. It dissolves potash and soda in their pure state; but appears to suffer some decomposition, probably from portions of its carbon and oxygen being combined by the resulting affinity the alkali exerts, so as to form carbonic acid; for the solution acquires a brown colour; and, according to Pelletier, carbonate of potash is formed, and the alkohol disappears *. Ammonia may be combined with it by distillation. Of the earths, strontites, and perhaps barytes, are dissolved by it.

The acids combine with it, and some of them decompose it; a particular order of compounds, Ethers, as they have been named, results from these actions, which will be better considered after the history of alkohol.

It unites with sulphur, but it is requisite that the sulphur should be presented in the state of vapour. In this way their combination was effected by Lauraguais †. According to Favre, if alkohol be highly rectified, it dissolves sulphur, merely by applying heat, lower than sufficient to cause the alkohol to boil. By digesting an ounce of alkohol with two drachms of sulphur, he found from 13 to 23 grains to be dissolved, according to the heat applied ‡. The compound of sulphur and alkohol formed by the process of Lauraguais, is a liquid of a reddish colour and fœtid smell, resembling that of sulphuretted hydrogen: it becomes turbid on cooling, and sulphur is precipitated from it by the addition of water. The proportion of sulphur it contains is about a sixtieth.

Phosphorus is dissolved by alkohol: the solution is rendered turbid, and the phosphorus precipitated on the affusion of water. When the liquor is poured on water, a tremulous vivid light is perceived, when the experiment is made in the dark.

Alkohol does not dissolve carbon, nor does it combine with hydrogen. It exerts no action on the metals, even when they are oxidated, but it dissolves a number of metallic salts.

It absorbs a number of the gases, some of them in larger, others in smaller quantities than those in which they are

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* Mémoires de Chimie, tom. i. p. 521.

† Mémoires de l'Acad. des Sciences, 1758, p. 84.

‡ Nicholson's Journal, vol. xiii. p. 70.

absorbed by water. The results with regard to this have been given in a table, along with those with regard to water, in the second volume.

Alkohol is the solvent of a number of vegetable principles, as sugar, resin, extract, camphor, essential oil, and several of the acids. With essential oils are formed the odoriferous essences and the distilled spirits. These are commonly prepared by distillation. A quantity of proof spirit is poured on any aromatic fragrant vegetable: a moderate heat is applied: the alkohol of the proof spirit dissolves the essential oil, and distils over. What are thus formed are named Distilled Spirits, in contradistinction to Distilled Waters, prepared by distilling water from the plant. As the essential oils are soluble in alkohol, the spirit may be impregnated with them by agitation.

Camphor dissolved in alkohol forms a compound, which is used in medicine as a stimulant. Resins dissolved in alkohol, form Varnishes. Balsams dissolve in it entirely, gum-resins partially.

Alkohol, from its power of dissolving these principles, is able to extract the active matter of many vegetables; and when diluted with an equal part of water, so as to form proof spirit, its solvent power is more extensive. Both in its pure and diluted state, it is frequently used in pharmacy to dissolve the active principles of vegetable products, and thus to separate them from inert matter with which they may be mixed. Solutions of this kind are named Tinctures or Elixirs. Those prepared with pure alkohol are decomposed by water, the resinous matter being precipitated; those with proof spirit, are in general miscible without decomposition.

The action of the more powerful acids on alkohol, it has been remarked, is peculiar, and gives rise to an order of compounds of some importance from their chemical properties. As produced by the different acids, they differ in their qualities: they agree, however, in the possession of certain general properties; are highly volatile, odorous, pungent, and inflammable; miscible with water, and capable of combining with alkohol in every proportion. These compounds are named ETHERS; the specific name of each being derived from the acid by which it is formed, as sulphuric, nitric, muriatic, or acetic ether.

SULPHURIC ETHER is of these compounds the one which has been longest known. The following is the process by which it is prepared.

Upon a quantity of alkohol in a retort, (selected thin at the bottom, so as to be capable of bearing a sudden heat), is poured an equal weight of sulphuric acid. The acid is added in a full stream, so that from its greater specific gravity it falls to the bottom of the retort; it is then mixed with the alkohol above by moderate agitation. The alkohol acquires a brownish colour; vapours having a fragrant odour are disengaged; and the temperature rises to about 180 of Fahrenheit. When the mixture is complete, heat is applied to the retort by the medium of a sand-bath. The liquor boils when the temperature is raised to 208, the ether being formed at that temperature, and distilling over: the condensation of it is promoted by keeping the receiver connected with the retort cool with water, and the distillation is continued till about half the quantity of the alkohol employed has distilled over, or until the neck of the retort becomes obscured with white fumes. If, to the residual liquid in the retort, there be added, when it has cooled, half the quantity of alkohol employed in the first distillation, on applying heat, a new production of ether takes place; and this may be repeated several times. In this way it was ascertained by Dollfuss, that one part of sulphuric acid can convert from two to three times its weight of alkohol into ether.

Besides ether, there are some other products formed during the action of sulphuric acid upon alkohol. Towards the end of the process an oily-like matter distils over, which has been named Oil of Wine. This can be obtained by changing the receiver: it is unctuous, thick, and less volatile than the ether, but is soluble both in it and in alkohol. It is obtained likewise by distilling sulphuric ether from a fresh quantity of acid; or by distilling a mixture of alkohol and sulphuric acid, in the proportion of one part of the former by weight to two of the latter. Chemists are not agreed respecting its nature: Fourcroy and Vauquelin consider it as similar to ether, and differing from that fluid principally in containing a larger proportion of carbon. Other chemists, particularly Higgins, have affirmed, that it is a compound of ether and sulphurous acid, and that by the addition of an alkali which combines with the acid, ether may be obtained from it. It does not appear, however, that this combination can be formed directly; and though it may contain a portion of acid, it is not improbable that it also differs from ether in ultimate composition.

At the same time that the oil of wine is formed, there is disengaged a quantity of olefiant gas: a quantity of carbonaceous matter somewhat bituminous, is also separated, which gives to the liquor a black colour. Towards the end of the process the liquor becomes so loaded with this, and is capable of bearing so high a temperature, that if the heat is kept up, the sulphuric acid is decomposed, and sulphurous acid gas and carbonic acid gas are produced. If care is not taken to keep the heat moderate, the whole liquor is apt to swell suddenly, and boil over into the receiver. If examined at this time, it is found to contain acetic and oxalic acids, and the sulphuric acid is considerably diluted with water.

From the formation of sulphurous acid towards the end of the process, the ether is so far impregnated with it, that it is rendered pungent and acrid. It is also diluted with a portion of water. It is purified by a second distillation with a very gentle heat applied by a water-bath, pure potash being previously added to it, in the proportion of two drachms to each pound; this attracts the sulphurous acid, and renders the water less volatile. Slaked lime may be substituted, as was proposed by Woolfe. Another method of rectification, proposed by Pelletier *, and revived by Dizé †, which I have found to succeed, is to distil the ether of the first distillation from a little black oxide of manganese, the oxygen of which combines with the sulphurous acid, converting it into sulphuric; and this, with the water, remains in the retort. Even after either of these processes, the ether may contain a portion of alkohol, which passes over in the first stage of the distillation. This is abstracted by agitation with water, which imbibes the alkohol, and a little of the ether: the greater part of the ether floats above, may be drawn off, and by distilling it with a very gentle heat, is obtained pure. Saussure found, that when a large quantity of it was burnt, and the water afforded by its combustion collected, not a trace of sulphuric acid could be discovered,—a proof that the acid is not necessary to its constitution ‡.

The formation of sulphuric ether had been ascribed by Lavoisier, in conformity to the antiphlogistic theory, to the acid communicating oxygen to the hydrogen of the alkohol, and forming water; thus subverting the balance of

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* Memoires de Chimie, tom. i. p. 516.

† Nicholson's Journal, 4to, vol. iii. p. 45.

‡ Both in the first distillation, and in the subsequent rectification of ether, rather a small receiver should be connected with the retort, as, from the great density of the vapour of ether, there is in a large receiver considerable loss.

attractions, and causing part of the carbon to be precipitated, while the remaining carbon, hydrogen, and oxygen, form the ether.

Fourcroy and Vauquelin, from a series of experiments which they undertook to elucidate this subject, affirmed, however, that the decomposition of the acid is not necessary: that although it may take place towards the end, when the liquor is loaded with carbon, there is no indication of it in the first stage, during which, principally, the ether is formed; no sulphurous acid gas is discharged, and if the process be stopt at the end of this stage, the remaining acid is capable of saturating the same quantity of alkali, as before its mixture with the alkohol *. They gave, therefore, a different view of this subject. They supposed, that the sulphuric acid acts only by the exertion of a disposing affinity, in producing the decomposition of the alkohol. By this affinity it causes part of the hydrogen and of the oxygen of the alkohol to combine and form water: the balance of attractions being subverted, a quantity of carbon is separated; and the remaining carbon, hydrogen, and oxygen, combine and form the ether.

Some doubts have been expressed with regard to the fact, whether the decomposition of the sulphuric acid is essential to the formation of ether or not. The proof of the residual liquor saturating as much of an alkali as the quantity of acid would do previous to its mixture with the alkohol, is not without fallacy, as, during the formation of ether, there is a formation from the elements of the alkohol, of some of the vegetable acids, particularly of the acetous†, which will contribute to the saturation of the alkali. In the formation of some other species of ether, the nitric for example, there is the undoubted decomposition

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* Nicholson's Journal, 4to, vol. i. p. 385.

† The oxalic acid has also been said to be formed, but, according to Vogel, this is not the case.

of the acid, and the communication of oxygen to the elements of the alkohol. And Laudet and Dabit published some experiments *, in which it appeared to be proved, that ether is formed when alkohol and black oxide of manganese are mixed and exposed to the proper heat, a very small quantity of sulphuric acid (as an ounce to a pound of alkohol) being added, merely to favour their action; and that muriatic acid heated with alkohol, gave no ether; while, if black oxide of manganese were added, an ether was formed. In opposition to these, however, Fourcroy and Vauquelin affirmed, that the liquors thus formed differ from ether in their constitution and properties †.

From the determination of the constitution of sulphuric ether by its analysis, a mode of investigation less exposed to error, the theory which Fourcroy and Vauquelin gave of its formation, appears to be nearly just. Its composition may be determined either from the products of its combustion, or from the products of its decomposition by heat. T. Saussure, in his first experimental investigation of the composition of alkohol and ether, employed the former of these methods, detonating the vapour of ether in a tube with oxygen gas, and finding the quantities of carbonic acid and water formed. From the results he assigned as the elements, carbon 59, oxygen 19, hydrogen 22, which gives a larger proportion of carbon and hydrogen, and a smaller proportion of oxygen, than what exists in the composition of alkohol ‡. In his subsequent investigation of the subject, he employed the same method as that which he used to determine the constitution of alkohol,—decomposition by transmission through an ignited tube, which of course led more directly to the discovery of the difference between them. The products were oxycarbu-

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* Annales de Chimie, tom. xxxiv. p. 282. 289.

† Ibid. tom. xxxiv. p. 318.

‡ Journal de Physique, tom. lxiv. Nicholson's Journal, vol. xxi.

retted hydrogen gas, and a small quantity of charcoal deposited, with an empyreumatic, oily, and bituminous matter, and part of this oil being apparently volatilized so as to occasion loss, rendered the precise determination of the results more difficult. The gas itself, however, amounted to nine-tenths of the ether decomposed, and hence its analysis led to a very nigh approximation of the composition. This gas, like that produced in the decomposition of alkohol, (page 371.) consumed in its combustion oxygen in the proportion of 3 volumes to 2 volumes of carbonic acid produced ;—the same therefore in this respect as olefiant gas; it afforded likewise a quantity of water, but less than that from alkohol. The gas from alkohol is represented by 2 of olefiant gas, and nearly 1 of water; that from ether by 3 of olefiant gas, and 1 of water in weight. From the results by detonation, Saussure inferred, that "ether is represented by the elements of 100 parts in weight of olefiant gas, and 25 parts of water." Pure alkohol, it has been already remarked, is represented by 100 of olefiant gas and 50 of water. Hence it follows, that the agency of sulphuric acid in converting alkohol into ether, consists in its causing an abstraction of the elements of water, no doubt by their formation, conformable to the theory of Fourcroy and Vauquelin : 100 parts of sulphuric ether of the specific gravity of 0.7155 at 68°, this being the state in which it was analysed by Saussure, consist, according to these results, of carbon 67.98, oxygen 17.62, hydrogen 14.40; and as ether has so weak an affinity to water, there is no reason to believe that it retains much of it in direct combination; of course not much of this oxygen and hydrogen exist in the state of water *. Gay Lussac, from these determinations, and from finding by experiment that the vapour of sulphuric ether is 2.586, has inferred, that it is composed of 2 volumes of

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* Journal de Physique, tom. lxxviii. Annals of Philosophy, vol. iv.

olefiant gas, and 1 volume of aqueous vapour, condensed into one volume [*].

Sulphuric Ether, highly rectified, is the lightest known liquid. It is obtained without difficulty of the specific gravity of .732, and by careful distillation has been brought so low as .716 at 65°. It is colourless and transparent; has a strong pungent taste, and a fragrant penetrating smell.

It is very volatile. It evaporates rapidly at the common temperature, and under the common pressure of the atmosphere. *In vacuo* it boils at a temperature below 32°: under the atmospheric pressure it boils at 98. In its spontaneous evaporation, a large quantity of caloric is absorbed, so as to produce cold: water inclosed in a small tube may be frozen, by ether evaporating from a piece of muslin wrapt round the external surface of the tube: and Dr. Higgins has observed, that in the rapid evaporation of ether, the temperature in frosty weather falls so low as —40. Ether congeals at —47.

From this volatility of ether, it enlarges the volume of any elastic fluid into which it is dropt; the volume at a common natural temperature being doubled, according to the observation of Priestley, who also observed, that the etherial vapour in this case could not be condensed by cold, but was absorbed by water. The specific gravity of the vapour of ether is according to Gay Lussac 2.586.

Ether is highly inflammable, and, when kindled, burns with a clear white flame, without any smoke, and without leaving any residuum, the products of its combustion being water and carbonic acid: the residual water generally gives indications of sulphuric acid, probably adventitious. From its high inflammability, its vapour diffused in the atmosphere takes fire; or if a drop or two of the ether be added to atmospheric air or oxygen gas, an explosion happens, on the contact of an ignited body. Mr Cruickshank found, that by agitating a little oxygen gas with sulphuric ether, the volume was doubled: in this state it did not explode; but when one part of it was added to three parts of oxygen, it exploded violently. It is also kindled by hyperoxymuriatic acid gas.

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[*] Annales de Chimie, tom. xcv. p. 315.

Sulphuric ether is soluble in water, but only in a limited proportion; the water taking up about a tenth part of highly rectified ether. When the proportion of ether exceeds, it holds on the other hand a little water dissolved. Ether is soluble in alkohol in every proportion.

Sulphuric ether exerts no sensible action on the fixed alkalis or earths. It unites with ammonia by distillation.

Neither does it act on the metals; but it is capable of decomposing the saline combinations of those that have a weak affinity to oxygen, by attracting that principle. Thus, muriate of gold dissolved in it is gradually decomposed, and the gold precipitated in its metallic form.

On the simple inflammables, its action is similar to that of alkohol. It dissolves sulphur, as Favre has shewn, one ounce of ether dissolving about twenty-five grains: the solution has a strong sulphureous smell and taste: it is less soluble in water than pure ether, and deposites sulphur as the ether volatilizes *. Ether likewise dissolves a small proportion of phosphorus: this solution, like the phosphuretted alkohol, is decomposed by water, but does not, like it, appear luminous during the decomposition.

Sulphuric ether is a solvent of many of the vegetable proximate principles, particularly essential oil, camphor, and resin. It is also the most powerful solvent of caoutchouc. In medicine, it is employed as a diffusible stimulant.

NITRIC ETHER. The action of nitric acid on alkohol is so violent, that the preparation of nitric ether is difficult.

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* Nicholson's Journal, vol. xiii. p. 69.

One part of the acid may be added gradually to three parts of alkohol without risk; after standing for some days, to admit of their reciprocal action, heat may be applied, and a portion of nitric ether distils over, with a quantity of unchanged alkohol. A preparation of this kind has been known in pharmacy, under the name of Sweet Spirit of Nitre. But wnen the proportion of acid is increased, the action becomes violent; elastic fluid is disengaged at each addition; and it requires particular arrangements to admit of so much acid being added as is sufficient to convert the whole alkohol into ether.

A method proposed by Navier is, to put into a strong earthen-ware bottle twelve parts of alkohol, and immerse it in water or ice; eight parts of nitrous acid are added in successive portions, mixing by agitation at each addition; the bottle is well corked, tied over, and put aside in a cool place. At the end of six days, the cork is to be perforated, to allow a quantity of gas retained by compression, to escape. The bottle is then uncorked, the liquid poured into a funnel, and the acid liquor beneath is allowed to run off from the ether which swims above. A similar method, less hazardous, was employed by Dr Black. He poured into a strong bottle six ounces of alkohol; then, by a funnel, the tube of which reached to the bottom of the bottle, two ounces of water were poured in gently, so that it did not mix with the alkohol, but raised it above it; and, lastly, four ounces of nitrous acid were added in the same manner, so that the column of water was interposed between it and the alkohol. The phial was set aside in a cool place: the water attracted the alkohol at the one surface, the acid at the other, and thus brought them gradually together, so as to admit of their reciprocal action without violence. At the end of a few months nitric ether was formed, and floated above the liquor, and might be withdrawn and rectified by distillation.

Other methods have been employed. The process of

Woulfe consists in connecting a high-necked tubulated retort or matrass with a receiver, connected by a tube with a range of tubulated bottles, in which water or alkohol is put; eight ounces of alkohol are poured into the retort, and six ounces of nitrous acid are added in successive portions. At each addition after the first, there is a disengagement of gas, and at the end of the operation nitric ether is found to have been formed and volatilized by the heat produced by the mutual action of the acid and alkohol: it is collected in the receiver, and may be rectified by mixing it with water, and distilling it. The alkohol in the bottles contains a portion of it also, and may be employed in a repetition of the process. Woulfe afterwards modified his process, by using alkohol, nitre, and sulphuric acid, four pounds of nitre being put into the retort, and a mixture of 4 lbs. of sulphuric acid, and 3 lbs. 5 ounces of alkohol, being added to it, in quantities not exceeding two ounces at a time, and only after the disengagement of elastic fluid from the previous addition has ceased. Pelletier has observed, that after repeating all the processes for the preparation of nitric ether, he found this to succeed best; nor could he discover in the product of it the most minute portion of sulphuric acid [*]. Thenard employed a process similar to the original one of Woulfe; he mixes equal weight of alkohol and nitric acid in a retort connected with a range of bottles, containing a saturated solution of muriate of soda, kept cool by a mixture of ice and salt, checking the action when it becomes violent, by pouring cold water on the retort. The gaseous product is transmitted through the liquor in the receivers: the nitric ether is thus condensed; it floats above the saline solution, is withdrawn, and freed from a portion of acid by agitation with lime. The incondensible gas is collected at the end of the apparatus in an inverted jar [†].

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[*] Mémoires de Chimie, tom. i. p. 99.

[†] Mémoires d'Arcueil, tom. i. p. 86.

The theory of the formation of nitric ether is even more obscure than that of sulphuric ether. It is sufficiently ascertained, however, that the acid is decomposed; nitric oxide gas is disengaged; and Pelletier found, that in following the process of Woulfe, the decomposition was complete, nitric acid not being discoverable, either in the liquor which passed over, or in the residuum. This appears, too, from some experiments by Bayen. He found that after digestion of one part of the acid with two of alkohol, for five weeks, the liquor was not capable of saturating half the quantity of an alkali that the acid previous to its mixture would have done: and if heat were applied, and the product and residual liquor mixed after distillation, the whole saturated only an eighth of the original quantity. And as a quantity of oxalic acid is formed in the process, it would contribute to this effect; so that nearly the whole of the nitric acid had suffered decomposition *. There is also in the formation of nitric ether a decomposition of the alkohol, as in the residual liquor oxalic and acetic acids are found, but there is no deposition of carbonaceous matter, as there is in the formation of sulphuric ether, the residual liquor being transparent, and of a light colour.

The theory of the formation of nitric ether has been more fully investigated by Thenard, in his experimental researches on the different ethers †. In its formation a large quantity of elastic fluid is disengaged, which has an etherial smell, is combustible, becomes slightly red when mixed with oxygen gas, precipitates but very slightly lime water, or barytic water, reddens strongly infusion of litmus, and dissolves rapidly in water, leaving only a small residue of nitrogen and nitric oxide. When passed through a series of bottles cooled by a mixture of ice and muriate of lime, it dimi-

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* Opuscules Chimiques, tom. 1. p. 584.

† Mémoires de la Société d'Arcueil, tom. i.
Nicholson's Journal, vol. xviii.

nishes greatly in volume, and deposites a considerable quantity of ether. When examined after this, it burns not slowly as before, but the combustion extends quickly through the whole mass; when agitated after combustion with water, a quantity is absorbed, and the remaining gas supports combustion. From these qualities Thenard infers, that this elastic fluid consists of a little nitrogen, nitric oxide, and carbonic acid gases; of larger proportions of ether, and nitrous oxide gas; and of a quantity of acid partly nitric partly acetic, which these gases hold dissolved, but so intimately combined with the ether, as not to be easily separated from it, even by the action of alkalis.

The nitric ether itself, obtained during the distillation in the liquid state, is always acid. This acid, partly nitric partly acetic, can be abstracted by agitation with lime; but what is singular, after this has been done, so that the ether does not redden litmus, it recovers acidity on distilling it, or on keeping it for some time. This Thenard found to be owing to the production both of nitrous and acetic acids; a proof that their elements enter into the composition of the ether even in its pure form.

By analysing pure nitric ether, by passing it through an ignited porcelain tube, Thenard obtained water with a little prussic acid, carbonic acid, a small quantity of carbonaceous matter, and a large quantity of elastic fluid, consisting of nitrogen, carbon, and hydrogen. From the known composition of the products of the decomposition, he infers, that 100 parts of nitric ether consist of 16.41 of nitrogen, 39.27 of carbon, 34.73 of oxygen, and 9.59 of hydrogen *.

From a comparison of all these facts, he infers, that the oxygen of the nitric acid combines with a large proportion

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* These proportions, in a subsequent memoir, he states at 14.49 of nitrogen, 28.65 of carbon, 48.52 of oxygen, and 8.54 of hydrogen.

of the hydrogen, and a small quantity of the carbon of the alkohol, whence result, 1*st*, Water and nitrous oxide, and small quantities of carbonic acid, nitrous acid, and nitric oxide; 2*dly*, The separation of a small quantity of nitrogen, and the formation of nitric ether by the combination in large quantity of the two elements of the nitric acid, with the alkohol from which the large proportion of hydrogen and small proportion of carbon have been abstracted; 3*dly*, The formation of acetic acid, by the combination, in certain proportions, of the hydrogen and carbon of the alkohol with the oxygen of the nitric acid.

Nitric ether has some resemblance in properties to sulphuric ether. It is light and volatile, and when pure, has these qualities even in a higher degree than sulphuric ether. It is inflammable, soluble in water and in alkohol. Its odour is strong, though scarcely so agreeable as that of sulphuric ether; in the state, however, of what has been named Dulcified Spirit of Nitre, it is more fragrant. Its colour is usually yellow; but this, as well as some of its other qualities, appears to be owing to the presence of nitrous acid. Thus, when kept, it continues to emit an elastic fluid, and tinges the cork of the phial yellow or red; and Deyeux found, that when one part of it is mixed with sixteen parts of water in a bottle with a tube, the nitric oxide gas which it contains is separated by a spontaneous effervescence.

Thenard having obtained it free from acid, and in a more concentrated state than that in which it had been formerly procured, has been better enabled to ascertain its properties. He found it to be so volatile that it instantly evaporates when poured out; bubbles of vapour rose from the mass of liquid, when the bottle containing it was held in the hand; and it boiled at the temperature of 70° under a medium atmospheric pressure; its odour is strong and penetrating; it is lighter than water, on the surface of which it floats like oil; it requires about 50 parts of water to dissolve it, but combines with alkohol in every proportion. It inflames easily, and burns with a white flame.

When equal parts of nitric acid and alkohol are mixed together, a strong effervescence takes place, and a gas is disengaged, which is slowly absorbed by water, explodes when mixed with oxygen and kindled, and is decomposed by sulphuric, nitric, and muriatic acids, which disengage from it nitric oxide gas. It has been named Nitrous Etherized Gas by the Dutch chemists, who first took notice of it, and was regarded by them as a compound of nitric ether and nitric oxide gas. Thenard regards it as a mixture of elastic fluids; and supposes that the greater part of the nitric oxide it affords when decomposed, arises from the decomposition of the nitric ether it contains.

Muriatic Ether. Chemists found it impracticable to form an ether by the action of muriatic acid on alkohol. By using, however, the acid in a state of combination with metallic oxides, they succeeded more or less completely in forming a product approaching in its properties to ether. And after the discovery of oxymuriatic acid, Scheele availed himself of it to attempt the formation of muriatic ether, by distilling muriatic acid from black oxide of manganese, receiving the gas in alkohol, and distilling this liquid with a very gentle heat. The success of this process, however, he found to be imperfect; and the product approached rather to an oil than a light ether. And Berthollet found, that though, by passing a current of oxymuriatic gas through alkohol, it was absorbed, and passed to the state of muriatic acid, while the alkohol acquired an odour of ether, which became stronger on a repetition of the process; yet, on repeating it a third and fourth time, this odour diminished, and at length was nearly lost, the liquor having rather the smell of vinegar; and on distilling it, after a small quantity of etherial liquor passed over, there was obtained only a watery liquor, which had the odour of burnt sugar; the residue had the same odour, and contained a quantity of acetic acid *.

Scheele had also distilled muriate of soda, oxide of manganese, sulphuric acid, and alkohol, to produce muriatic ether; and a similar process was employed by Pelletier †; but the success of it does not appear to have been greater. Pelletier observed, that in adding an alkali to the etherial liquor obtained by his process, an oily matter separates, which floats on the residual liquor. According to Van Mons, this oil is produced by the action of an excess of oxymuriatic acid on the muriatic ether; and it is from this circumstance, he affirms, that muriatic ether cannot be formed in sensible quantity by the process of Scheele and Pelletier, so that if this action is prevented by putting an alkaline solution into the bottles in which the product is condensed, muriatic ether is obtained ‡.

Boss likewise observed, that, by the usual process with oxymuriatic acid, muriatic ether could not be formed, but only a heavy oily fluid: And he affirmed, what now appears to be the case, that it may be formed from muriatic acid. His process is to pass a current of muriatic acid gas from 20 ounces of perfectly dry muriate of soda, and 10 ounces of sulphuric acid, gradually mixed, in a retort, through 10 ounces of highly rectified alkohol, kept cool. The alkohol thus charged with acid is distilled to one half; the distilled liquor is agitated with an alkaline solution, to remove any superfluous acid; and the liquid which floats above is the muriatic ether ||.

This subject has been investigated by Thenard §, who has

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* Mémoires de l'Acad. des Sciences, 1785, p. 509.

† Mémoires de Chimie, tom. i. p. 142.

‡ Philosophical Magazine, vol. vii. p. 48.

|| Nicholson's Journal, vol. v. p. 221.

§ Mémoires de la Société d'Arcueil, tom. i. p. 115. 557. Nicholson's Journal, vol. xviii.

pointed out the causes of the want of success in the former attempts. When the acid and the alkohol are presented to each other in the elastic form, their elasticity is an obstacle to their intimate action. When they are mixed in the liquid state, if a strong heat is applied, the rarefaction opposes the combinations that would otherwise be established; and, at a low heat, they remain mixed without forming ether. It is by preserving a medium between these that the operation succeeds. The proper muriatic ether exists too, except at low temperatures, in the gaseous state; and hence, even when it was produced in former processes, the greater part of it was lost, without the loss being perceived. The following is the process which Thenard gives.

There are put into a retort, of a capacity not greater than what holds the mixture in the body of it, equal parts by measure of muriatic acid and alkohol, each in the highest state of concentration; they are well mixed, and a few grains of sand are put in, to prevent the sudden ebullitions that might happen in the course of the process. The retort is exposed to the naked fire of a common furnace, supported on a grate of iron wire, there being adapted to it a Welther's tube of safety, terminating in a three-necked bottle, the capacity of which is double that of the retort, and which is half filled with water. The safety tube is to be immersed in the water 2 or 3 inches; a straight tube is inserted in the middle orifice of the bottle, and a curved tube proceeds from the other, which terminates under an inverted phial filled with water. The heat is applied to the retort gradually, and when the liquor is brought to boil, muriatic ether gas is abundantly formed. If the production of gas cease, more may be obtained by adding fresh alkohol. The whole success of the operation depends on the due regulation of the heat, as, if it is either too high or too low, little ether is formed.

Muriatic ether, thus obtained in the state of gas, is colourless; its odour is etherial, and its taste saccharine. It produces no change on infusion of litmus, syrup of violets, or lime water. Its specific gravity, compared with that of atmospheric air, is 2.219, under a mean pressure, and at 63° of Fahrenheit. Under this pressure and temperature, water dissolves its own volume of it. Under the same pressure, but at a temperature of 50, the gas becomes liquid, and is obtained in that state in the process for forming it, by causing it to pass through long narrow vessels, dry, and surrounded with ice.

Liquid muriatic ether is limpid; it has no action on litmus, or syrup of violets; its odour is strong, and its taste similar to that of sugar. Poured on the hand, it passes into ebullition, producing a considerable degree of cold. Its specific gravity is to that of water, at the temperature of 39° of Fahrenheit, as 874 to 1000. It does not congeal at a temperature of —22°.

Some singular facts are presented in the chemical constitution of this ether. No muriatic acid can be detected in it; it does not redden litmus; the alkalis have no action on it; and the solution of silver is not rendered turbid by it. But when it is kindled, such a quantity of muriatic acid is produced or set free, as to be apparent by its fumes and suffocating odour, and to precipitate a strong solution of nitrate of silver in a solid mass.

Thenard found, however, in subsequent researches, that though muriatic acid is not immediately discovered, yet, if time be allowed, it appears. The alkalis, or the nitrate of silver, after some days mixture with it, attract a small portion of the acid, and still more after two or three months; though even at the end of that period the quantity is inconsiderable. The acids in the cold produce no change in this ether; but if, in the state of gas, it be passed through sulphuric or nitric acid, nearly at a boiling heat, it is decomposed, and much muriatic acid is set free. The same facts have been established by Boullay.

From the quantity of acid which disappears in the formation of a given quantity of muriatic ether, and from the products of the combustion of the etherial gas, Thenard endeavoured to determine the proportions of its elements. Those he assigns are 51.39 of carbon, 33.03 of oxygen, and 15.08 of hydrogen, forming 100 parts of a compound, with which are combined 41.72 of muriatic acid, forming 141.72 of muriatic ether. It does not appear clearly whether the alkohol exists in it undecomposed or not: there is no sensible precipitation of carbonaceous matter, and therefore all or nearly all the carbon of the alkohol must exist in the ether. But it is uncertain whether this is the case too with the hydrogen and oxygen, or whether portions of these combine and form part of the water of the residual liquor. The state of the acid is not less uncertain, whether it exists as such in the ether, or whether its elements only enter into the composition, and, of course, when the ether is burnt, or otherwise decomposed, the acid is reproduced. To solve these questions, Thenard decomposed the gas, by transmitting it through an ignited tube; and he obtained, as nearly as could be expected, all the acid which had gone to the formation of the quantity decomposed. It is therefore not merely the base of the acid that exists in the composition of the acid, but all its elements; but whether these are in simultaneous combination with the other elements of the ether, or whether they exist in it as muriatic acid, is not apparent. The former, Thenard remarked, might be regarded as more probable, from the consideration, that if the acid be supposed to exist in the ether, it must be concluded, what is improbable, that alkohol, or the elements of alkohol, act on muriatic acid with more energy than even the alkalis can, since these only decompose it slowly and partially; and also from the improbability of the circumstance, that nitrate of silver, which abstracts muriatic acid from all its combinations, should not separate it from this ether, if it existed in it, or separate a small part only after a long time. In his subsequent researches, however, on the action of acids on vegetable matter, he has maintained the opinion, that a number of vegetable substances combine with acids, and neutralize their properties nearly as alkalis do; and this view of the relation of acids to vegetable matter, leads to the conclusion, that the acid exists fully formed in muriatic ether. Robiquet and Colin have lately inferred, that muriatic ether is a compound of muriatic gas and olefiant gas, equal volumes of each condensed into one volume. The oily matter procured from the action of oxymuriatic gas on olefiant gas, it has already been stated, they consider as a compound of equal volumes of these gases condensed into one volume *.

Thenard examined the processes which had been formerly employed to form muriatic ether, particularly those in which the oxygenized metallic muriates are made to act on alkohol. With muriate of tin, he found, that only a small quantity of ether is formed, and this he supposes is from the action of the excess of acid in the metallic muriate. With oxymuriatic acid no ether was formed; there was only the production of the oily-like matter observed by Scheele, partly pure, and in part dissolved by alkohol. The production of this is accompanied with the formation of water and carbonic acid, and the separation of a little carbonaceous matter. The oily matter is white, has a cool penetrating taste, and a peculiar odour, not etherial; it is heavier than water and more volatile; it is soluble in water in small proportion, and is abundantly soluble in alkohol. Thenard considers it as a compound of muriatic acid with a species of vegetable matter, and as one of a numerous series of compounds in which vegetable matter neutralizes acidity.

It appears from these researches, that muriatic ether had not been before known to chemists in its pure form. The-

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* Annales de Chimie et Physique, tom. i.

nard has remarked, however, that Gehlen had formed it, by distilling a mixture of concentrated muriate of tin and alkohol, and a mixture of muriate of soda, alkohol, and sulphuric acid; he had even described its principal properties, but without having investigated its constitution.

Boudet has given a process for the preparation of PHOSPHORIC ETHER. He mixed liquid phosphoric acid of a thick consistence and alkohol in equal proportions, in a tubulated retort, connected with a receiver and an Woulfe's bottle filled two-thirds with lime-water: heat was applied, so as to cause the mixture to boil; a portion of unchanged alkohol first distilled; this was succeeded by a liquor having an etherial odour, which reddened slightly the syrup of violets: when rectified by distillation, from carbonate of magnesia, the product was colourless, and had an odour similar to that of sulphuric ether: it was volatile and inflammable, it's combustion not being accompanied with any smoke. It floated on the surface of water, but by agitation with it, was dissolved. It dissolved the volatile oils, and also phosphorus. Its specific gravity was to that of alkohol, as 94 to 100. After its production, when the heat was much raised, a quantity of oily matter distilled over, and carburetted hydrogen was disengaged. The residual liquor was brown, and contained much phosphoric acid *.

Another process was described by Boullay †. It consists in dropping alkohol on an equal weight of phosphoric acid of the consistence of honey, previously heated to 246 of Fahrenheit. The mixture takes place with violence and ebullition. A receiver being connected with the retort, which is kept cold by a mixture of ice and salt, distillation is performed. Alkohol passes over, with an etherial fluid, a portion of water, an oily-like fluid, and a liquid

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* Annales de Chimie, tom. xl. p. 125.

† Nicholson's Journal, 8vo, vol. xviii. p. 65.

of an extremely fœtid smell, which reddens litmus from the presence of acetic acid. The two first products being collected, are rectified by distillation from dried muriate of lime. A liquid is thus procured, which in smell and taste has the greatest resemblance to sulphuric ether, is of the same specific gravity, dissolves in 8 or 10 parts of water, evaporates quickly, boils at 100°, and burns with a whitish flame, leaving a carbonaceous residuum without any trace of acid. Phosphoric ether therefore resembles sulphuric ether, in containing none of the acid employed in its preparation: and hence, ethers appear to form two classes, one including those formed from the fixed acids, the sulphuric and phosphoric, the acid only causing their production without entering into the composition of the product; the other comprehending the ethers formed by the volatile acids, into the composition of which a portion of the acid seems always to enter.

Fluoric Ether has been said to be formed by putting fluate of lime, previously ignited and in powder, into a retort, with equal weights of alkohol and sulphuric acid, and distilling to dryness. The product of this distillation being distilled to one half, and a portion of acid abstracted from it by a solution of potash, on being again distilled, afforded an ether of the specific gravity of 0.720, which burnt with a blue flame, and had a bitter taste. It resembles sulphuric ether; and it is not improbable, that it may be this ether disguised *.

Acetic Ether has been known for a considerable time, Lauraguais having given in 1759 the process for preparing it, by distilling alkohol with the concentrated acetic acid procured by the decomposition of acetate of copper by heat. Scheele affirmed, that it cannot be formed without the intervention of a mineral acid; but Pelletier observed, that it is procured with certainty, by distilling alkohol repeat-

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* Nicholson's Journal, vol. viii. p. 145.

edly from the acetic acid. The alkohol at first acquires an etherial odour, but is miscible with water; by returning it on the residual liquor, distilling it, and repeating this for a third time, this odour becomes stronger: the acid contained in the product is saturated by adding carbonate of potash; and, by distillation, there is procured a pure acetic ether, in quantity about half of the alkohol employed *. Henry has also proved, that this process succeeds perfectly †, and Thenard has obtained by it an acetic ether. According to Pelletier, acetic ether may likewise be formed by distillation, from a mixture of sulphuric acid, acetate of copper, and alkohol; and Henry found the ether thus produced to be the same as that obtained by the preceding process. According to Laplanche, it may also be obtained from a mixture of sulphuric acid, alkohol, and acetate of lead.

In the formation of acetic ether by the first of these processes, Thenard found, that if the distillation of the two ingredients be repeated a sufficient number of times, nearly the whole alkohol is converted into ether, and a great part of the acetic acid is decomposed. He concludes, that acetic ether consists of the principles of the acid, or rather of the acid itself united with those of the alkohol, without the formation of any other compound ‡. Though it is formed by the action of acetic acid alone, it is produced, he found, with more facility when a portion of a mineral acid is added. From a mixture of 30 parts of alkohol, 20 of acetic acid, and 5 of sulphuric acid, it is formed almost without heat, nearly the whole of the acetic acid disappears, and the etherial product is easily rectified by distillation from potash. Nitric and muriatic acids have a similar effect, but require to be used in a larger proportion; phosphoric

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* Mémoires de Chimie, tom. i. p. 237.

† Nicholson's Journal, vol. xvii. p. 219.

‡ Mémoires de la Société d'Arcueil, tom. i. p. 158.

acid, as it is not soluble in alkohol, does not succeed, but the phosphorous acid does with considerable facility; and the effect in all these cases appears to be owing to the mineral acid condensing the alkohol, and thus subjecting it to the action of the acetic acid, which combines with it *.

Acetic ether has an agreeable odour, etherial, but in which the smell of acetic acid is perceptible; its taste is peculiar; its specific gravity is 866. It evaporates when exposed to the air, and boils at 128°. It burns with a yellowish white flame; acetic acid appears during the combustion; yet no acidity can be discovered by the test of litmus in the ether itself. It is soluble in water, requiring about 7½ times its weight for its solution. In this aqueous solution no acid is developed; but if an alkali be added, the odour and taste of the ether disappear, and the alkali is saturated; after this, if it be subjected to distillation, alkohol much diluted is obtained, and the acetate of the alkali employed remains; a presumptive proof of the theory of the constitution of this ether given by Thenard.

Thenard has examined the action of the other vegetable acids on alkohol, to ascertain if they form ethers. The tartaric, citric, malic, benzoic, oxalic, and gallic acids, dissolve in it, but they produce no chemical change, however frequently the alkohol may be distilled from them.

If alkohol, however, be subjected at the same time to the action of the vegetable acids, and of a mineral acid, as the muriatic or sulphuric, new combinations are established, as Thenard has shewn †, and products are formed in which the vegetable acid exists with its properties neutralized, but without any of the mineral acid in the composition. The latter appears therefore by condensing the alkohol to favour its action on the vegetable acid; and this action, Thenard concludes, is that of neutralizing it, near-

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* Mémoires d'Arcueil, tom. ii. p. 16.

† Ibid. p. 8.

ly as acidity is neutralized by an alkaline base. These products can scarcely be regarded as of an etherial nature. That obtained by the action of benzoic acid, aided by muriatic acid, on alkohol, Thenard found, when freed from free benzoic acid, to be of an oily appearance, heavier than water, acrid and volatile; nearly insoluble in cold water, but somewhat soluble in hot water, and soluble in alkohol. The products from oxalic, citric, and malic acids, their action on alkohol being aided by sulphuric acid, are of a similar nature,—oily in appearance, imperfectly soluble in water, and soluble in alkohol. That from tartaric acid is of the consistence of syrup. These substances are decomposed, though with difficulty, by the alkalis, and the vegetable acid from which they have been formed, is obtained in combination with the alkali.

To the vinous fermentation probably belongs that fermentation which takes place in the raising of bread. A small quantity of yeast is mixed with the flour; or a quantity of the flour of wheat is mixed with hot water, allowed to stand for a day or two, and is then used as a ferment. A portion of it, or of the yeast, is mixed with flour into a soft paste, and is kept in a warm place; it swells, becomes spongy from the extrication of air, and, were the fermentation allowed to continue, would become sour. A small quantity of this leaven, as it is named, is mixed with the dough from which the bread is to be baked: fermentation is thus excited, and the gas extricated raises the dough. It is checked by the baking; but its effects remain, and give rise to the sponginess and lightness of well-baked bread. The bread fermented with yeast is less liable to become sour than where the ferment from flour merely is used.

Though some chemists have considered this as a peculiar species of fermentation, there can be little doubt that it is analogous to the vinous. Dr Pennington had denied this, from finding, that, on submitting dough to the action of yeast for three quarters of an hour, and then subjecting it to distillation, it gave merely water, without any spirit. But, as Mr Collier remarked, this can only prove, that a complete fermentation is not necessary to raise bread. It may proceed so far as to produce that effect, by the extrication of carbonic acid, and yet not fully convert the fecula into alkohol. And he found, that, on subjecting wort for the same length of time to the action of yeast, though it exhibited every sign of fermentation, it gave no spirit by distillation *. That it is the vinous fermentation which occurs, is also proved by the fact, that, if not checked, it runs into the next stage of fermentation, the acetous, as is evident from the bread becoming sour, and from its peculiar smell in this state. It is curious that new flour does not afford bread of such good quality as that which has been kept some months. The flour of grain too, which has suffered incipient germination, is much inferior in the quality of the bread prepared from it: and from this principally appears to arise the injury which wheat sustains from a wet harvest. Various methods have been employed to remedy the imperfections of bread from inferior flour, such as washing the grain with hot water if it is musty, proposed by Mr Hatchet; drying and heating it even to a certain extent; adding various substances, such as magnesia, &c. Some experiments on this subject have been given by Mr E. Davy, and by a Commission of the Academy of Sciences †.

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* Manchester Memoirs, vol. v. p. 255.

† Philosophical Magazine, vol. xlviii. p. 458. vol. xlix. p. 161. 173. 191.

SECT. II.—OF THE ACETOUS FERMENTATION.

IF liquors which have undergone the vinous fermentation be kept at a temperature not much below 60°, and with the air not entirely excluded, they gradually suffer another change; they lose their vinous flavour, pungency, and intoxicating quality, and become sour. Chemists have considered this as a second stage in the general process of fermentation; have named it the Acetous; and the product forms Vinegar or Acetic acid.

Not only do vinous liquors suffer this change, but every substance susceptible of the vinous can pass into the acetous fermentation. Hence, sugar, dissolved in water, sweet vegetable juices, or infusions of grain that have been malted, can be converted into vinegar. Fecula, even without the previous process of malting, is susceptible of it: for, in the process of starch-making, a quantity of vinegar is formed, not merely from the small portion of saccharine matter in the grain, but likewise, as Vauquelin, in his analysis of the sour liquors of the starch-makers, has remarked, from the fecula itself*. Even substances which are not susceptible of the vinous fermentation, may suffer the acetous. The contrary opinion was indeed formerly maintained, the acetous being regarded as a continuance of the vinous fermentation, and as necessarily preceded by it. But it often happens where the former cannot be traced, and where there is no reason to suppose that it ever did exist, as in vegetable juices or infusions containing mucilaginous with scarcely any saccharine matter.

Nor is pure alkohol, in any state of dilution, capable of undergoing the acetous fermentation; there must be present other vegetable principles, as sugar, mucilage, or farinaceous matter. Even a certain proportion of these is requisite. Hence strong wines do not become so readily sour as weak wines; for the same reason wine that has been clarified is less liable to ferment; and strong wines can be made to pass into the acetous fermentation more easily, by adding to them sugar or mucilage. Even the vegetable acids appear to contribute to it, and in the conversion of sweet vegetable juices into vinegar, there is reason to believe that the malic and tartaric acids they contain pass into the acetic acid.

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* Annales de Chimie, tom. xxxviii. p. 261.

The addition of some substances which act as ferments, is also requisite. It is true, that wine and other fermented liquors become sour; but this is from their containing a portion of matter analogous to ferment, which excites the change. In preparing vinegar, it is known that a certain quantity of such matter, deposited from a liquor that has previously passed into vinegar, or a quantity of yeast, must be added; and there is reason to believe, that it is vegetable gluten which is the essential principle of these ferments. Fourcroy and Vauquelin found, that when sugar was added to water which had stood over the gluten of wheat, it quickly formed vinegar; and Berthollet obtained the same result from a mixture of gluten and starch *. This principle, Vauquelin remarks, contributes to the formation of vinegar in the liquor formed in the manufacture of starch; and the matter contained in common vinegar from malted grain, which renders it so liable to a kind of putrefaction, is, according to this chemist, vegetable gluten.

The admission of atmospheric air is essential to the acetous fermentation. Hence wines that are well bottled may be kept a long time uninjured, while the more free the exposure to the air is, they become the sooner sour. The

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* Annales du Museum National, tom. vii.

oxygen of the air is absorbed. According to Saussure, it does not enter into the composition of the acetic acid, but is expended in abstracting carbon, and forming carbonic acid. In keeping wine in contact with oxygen gas for a year in receivers closed with mercury, he found it converted into vinegar; but the diminution of the volume of the gas never exceeded, but was inferior to, the volume of the wine; hence, as he inferred, the oxygen had combined with carbon so as to form carbonic acid, which had been absorbed by the liquor. And he found, that when he made the experiment with wine previously impregnated with carbonic acid gas, this wine, under the same circumstances, was equally converted into vinegar, but without the volume of the elastic fluid above it being changed; the oxygen consumed being replaced by an equal volume of carbonic acid gas*.

A certain temperature is requisite to the acetous fermentation. It takes place slowly, below 60; but it proceeds with more rapidity between 60 and 80; and in forming vinegar artificially, the temperature is kept high. If it fall below 50, it is checked; hence wines can be longer preserved by being kept below this temperature.

The phenomena which occur in the acetous fermentation are analogous to those in the vinous. When it is proceeding rapidly, there is an intestine motion, not accompanied, however, with such a disengagement of elastic fluid as in the vinous fermentation; the liquor is turbid, and its temperature rises; its smell becomes acetous. These appearances at length subside, and the liquor gradually becomes clear, having deposited a kind of glutinous sediment similar to yeast.

The theory of the acetous fermentation is not completely elucidated. Since the strength of the acid formed by it is proportional to the quantity of alkohol, or of matter of a composition analogous to alkohol, and since this alkohol disappears during the fermentation, Lavoisier supposed that the theory of the process might be inferred from the changes which this principle can be supposed to suffer; and, as he found that oxygen is absorbed, while scarcely any sensible quantity of carbonic acid is extricated, he concluded, that the acetous fermentation consists in the oxygenation of the alkohol. If the experiments of Saussure be correct, in proving that as much carbonic acid is formed as corresponds with the quantity of oxygen consumed, the theory of Lavoisier would require to be so far modified, as to ascribe the change of alkohol into vinegar rather to the abstraction of carbon than the fixation of oxygen; thus leaving a larger proportion of the latter principle in the composition of the acetic acid.

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* Recherches Chimiques, p. 144.

This view cannot, however, be received as altogether just, since alkohol alone cannot undergo this change, nor can it by oxygenation be converted into acetic acid; and since the presence of mucilage, saccharine matter, or other principles, is always necessary to the acetous fermentation, the operation of which is not explained by the theory. Neither does it explain the action of the ferment, which appears to be equally indispensable. If nitrogen enters into the composition of acetic acid, as has been supposed, the operation of the ferment may be partly that of affording this element. The series of changes in the acetous appear to be similar to those in the vinous fermentation, only that from the action of the oxygen of the atmospheric air, a more oxygenated product is formed, whence probably its acidity.

Vinegar, the product of the acetous fermentation, is prepared in different countries from different materials. Where the grape is cultivated, it is obtained from weak or sour wine. This is kept in a proper temperature with the access of the air, and the fermentation is excited by the addition of a quantity of the sediment of vinegar, of wine already sour, or of the lees of such wine. The product is stronger in proportion to the previous strength of the wine. In this country it is prepared from unrefined sugar, or from the wort obtained by infusion from malted grain; the fermentation being excited by yeast. This vinegar is inferior in strength and purity to that from wine, and is more liable to become mouldy, or suffer the putrefactive fermentation. This appears to be owing to the presence of glutinous matter; hence the rationale of the method which Scheele pointed out for preserving vinegar, that of heating it, and bringing it to boil for a few minutes, the glutinous matter being separated by a kind of coagulation.

Vinegar, fully fermented, is limpid, of a yellow or reddish colour, having an odour agreeable, and pungent, and a sour taste. It differs, in strength and purity, as prepared from different materials. The real acid is combined with much water; and with this there are portions of gluten, mucilage, sugar, and extractive matter, from which it derives colour, and frequently some of the vegetable acids, particularly the malic and tartaric.

The acid which exists in vinegar, is formed in other chemical processes than fermentation. It is produced in the liquor in which wheat is macerated in the formation of starch: it appears frequently where vegetable matter has been acted on by sulphuric, or nitric acid, as in the preparation of ether, and in a number of analogous operations; and it is produced in the distillation of wood and the decomposition of many vegetable substances by heat. The process of decomposing wood by heat to afford it, is carried on with advantage on a large scale, to obtain it for several uses to which it is applied, particularly the preparation of different metallic acetates used in the arts; and this more especially as the charcoal which is the residuum is superior in quality to that prepared by the common process *. A very strong vinegar is accordingly now obtained in this way, which is rendered by distillation from charcoal, perfectly pure, and free from all empyreumatic smell, so as to be much superior to common vinegar, for economical purposes.

From vinegar the pure acid is procured with most facility. The simplest method is by distillation. A quantity of common vinegar is distilled in a retort with a sand heat, or in a tin still with the fuel directly applied. The first portion that passes over, to the amount of about $\frac{1}{8}$ of the vinegar, is little more than water, slightly acidulated: what passes next is more acid, and forms the distilled vinegar. When about $\frac{2}{3}$ have been distilled, the residual liquor becomes so loaded with extractive matter, and requires so high a temperature to keep it boiling, that were the distillation continued it would be scorched, and the distilled liquor would acquire an unpleasant empyreumatic odour. This liquor, however, is strongly acid, even more so than what has passed over. If the receiver be changed, this strong acid may be distilled, and can be applied to some uses; or by adding to the residual liquor a portion of water, the distillation may be recommenced, and a fluid similar to what has been collected be obtained. Or if a tin still be employed, the same purpose is attained by adding portions of warm water during the distillation. At the end of the operation, there remains a liquor of a deep red colour, very empyreumatic, and which on standing deposites supertartrate of potash. The extractive matter, when urged with a strong fire, yields the usual products of vegetable matter, with a portion of ammonia.

Distilled vinegar is limpid and colourless. Its odour is fainter and less pleasant than that of common vinegar; its

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* Annales de Chimie, tom. lxvi.

taste less sour, and its acid powers are weaker. It is purer, however, and is not liable to decomposition on keeping. It is principally used in pharmacy.

Vinegar can be concentrated by freezing: the congelation takes place at a temperature below 28° ; the congealed part is ice, leaving of course a stronger acid. If the process be performed on distilled vinegar, a very pure acid is obtained. The method Lowitz recommended is, to freeze a large quantity of vinegar, and distil the unfrozen part in a water-bath ; the distilled vinegar thus procured is again congealed, and the liquid portion is lastly distilled from charcoal powder. A highly concentrated acid, of an agreeable odour, is obtained. If it be exposed to a very intense cold, equal to —38°, it shoots into crystals; when the fluid part is withdrawn, the crystals liquefy when the temperature rises, and the liquid is limpid as water, extremely strong, and has a highly pungent acetous odour. This is the pure acid, any foreign matter remaining in the uncongealed liquid. Lowitz obtained the acid equally strong, by taking vinegar which has been once congealed and distilled, mixing it with a large quantity of charcoal powder, and distilling from a retort in a water-bath ; a weak acid comes over : the retort is then placed in a sand-bath, and urged with a strong fire, as long as any fluid distils quickly : stopping it when it begins to distil more slowly, as it is then principally water. The distilled acid may be concentrated by freezing, the uncongealed portion being poured off from the strong crystallized acid *. It is singular, that the acid concentrated by freezing acquires an unpleasant odour ; from which it is freed by distillation from charcoal.

Other methods are employed to obtain the concentrated acid. Distilled vinegar is combined with an alkali or

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* Crell's Chemical Journal, vol. i. p. 242.

earth, and the concrete neutral salt is decomposed by an acid. The process of Westendorf, is to saturate soda with distilled vinegar; obtain the acetate by crystallization, and pour upon it, in a retort, half its weight of sulphuric acid. By applying heat, the acetic acid is distilled over; and should there be sulphuric acid mixed with it, it may be distilled a second time from a little acetate of soda. According to Lowitz, a preferable method is to mix three parts of acetate of soda with eight parts of super-sulphate of potash, both salts being dry and in fine powder, and to distil from this mixture, in a retort with a gentle heat.

It was also known, that from certain metallic salts, formed from vinegar, a strong acid could be procured by distillation. The salt usually employed, is that formed by the action of vinegar on copper, the Verdigris of commerce. It is reduced to a fine powder, which is dried by a moderate heat. This is introduced into a retort, and urged with a fire gradually raised: the portion that first comes over is weak, and is removed; it is succeeded by an acid liquor extremely strong, and having a pungent odour. As obtained by the first distillation, it holds a small quantity of oxide of copper dissolved, from which it may be freed by a second distillation, with a more gentle heat. The acid procured by this process, had formerly the name of Radical vinegar.

This acid was observed to differ in several of its properties, and in its combinations, from the acid which exists in distilled vinegar, concentrated by freezing; hence the opinion was maintained, that there is an essential difference between them. Berthollet having concentrated distilled vinegar by freezing, and brought the acid obtained from verdigris by heat, to the same specific gravity by dilution, observed, that the latter had a taste and odour more pungent than the former; it appeared to exert a stronger attraction to the alkalis, and to form with them combinations more intimate, and differing in their properties from those formed by the other *. The difference he supposed owing to oxygen being received by the acid from the oxide of copper. The two acids thus came to be regarded as differing in degree of oxygenation, and were distinguished by the names of Acetous and Acetic Acids.

Adet called this opinion in question. Examining the products of the decomposition of acetate of copper by heat, he found reason to conclude, that the acid expelled from it receives no oxygen from the oxide, but is the same as that in the salt, except that it contains less water. He compared it, too, with the acid disengaged by sulphuric acid from acetate of copper, and acetate of potash, and found them the same. And in examining the actions of these acids on a number of substances, metallic, earthy, and alkaline, and the compounds they form, he found them identical, and equally so, allowing for the dilution, with distilled vinegar. He concluded, therefore, that the acetic acid, expelled by heat from its metallic salts, does not differ essentially from the acetous, and that the apparent differences between the two, arise from the one being a little weaker than the other †. Gren held the same opinion.

Chaptal maintained the opinion, that there is a difference between these two states of acetic acid; but he regarded this as depending, not on a different degree of oxygenation, but on a different proportion of carbon: the acetous acid existing in verdigris, losing, when it is expelled by heat, a portion of its carbon, which is attracted partly by the oxygen of the metallic oxide, partly by the oxide itself ‡. A similar view had been advanced by Perés; while Dabit endeavoured to support the first opinion, that these

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* Mémoires de l'Acad. des Sciences, 1783, p. 403.

† Annales de Chimie, tom. xxvii. p. 299.

‡ Nicholson's Journal, 4to, vol. ii. p. 518.

acids are in a different degree of oxygenation [*]. Darracq again examined the subject. He repeated the experiments of Adet, and found them correct; and added others, from which it resulted, that when the two acids are brought to the same specific gravity, there is scarcely any difference between them in their physical properties, except that the smell of the acetic is a little empyreumatic. Their chemical properties are alike, and their combinations the same. The acetous, submitted to the action of substances capable of affording to it oxygen, was not changed: nor by analysis did they afford different proportions of charcoal. Common vinegar, however, contains a quantity of mucilaginous or extractive matter, which Darracq found to be not altogether separated from it by distillation, and a portion of which even adheres to the acid in its saline combinations. The presence of this, in what has been named Acetous Acid, disguises its properties a little; but by distilling the acid repeatedly from muriate of lime, an acid is obtained equally strong with the acetic, and having an odour as pungent and not empyreumatic [†]. In the usual processes by which what has been named acetic acid is obtained, a product is formed, as is immediately to be stated, somewhat spirituous, which appears, to a certain extent, to modify the properties of the acid, and in particular to diminish its specific gravity, and give it inflammability and a higher degree of volatility.

There exists, then, only one acid of vinegar, which, in conformity to the principles of the modern nomenclature, is named the Acetic. Its salts must be denominated Acetates; and the salts named Acetites, as distinct from these, have no existence.

Acetic acid is extracted from the metallic salts in which it exists, by other methods than by the application of heat; in particular, by employing the affinity of a fixed acid to disengage it. It can thus be obtained from acetate of lead, by the intervention of sulphate of copper or of iron, a mixture of equal parts of dry sulphate of iron, and acetate of lead, being exposed to heat in a retort, as long as any acid comes over. The acid thus procured, however, is weaker, and, according to the observation of Debuc, confirmed by the experiments of Planche and Boullay, contains sulphurous acid; this may be abstracted by distilling it from black oxide of manganese, mixed with a small quantity of carbonate of potash *.

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[*] Philosophical Magazine, vol. x. p. 354.

[†] Ibid. vol. xiii. p. 12.

In the production of acetic acid by these processes, a portion of the product appears to be of an etherial nature. When strong vinegar is distilled, the fluid that first passes over has been observed to be weakly spirituous; this probably arises, however, from alkohol contained in the vinegar. But in the decomposition of the acetates, such as the acetate of copper by heat, a spirituous product appears to be formed. Derosne observed, that the acid at different stages of this process, differs in specific gravity and in acidity; these however are not proportional, and hence cannot be ascribed to the degree of concentration of a uniform product: the inferior specific gravity of the lighter portions, he supposed owing to the production of a substance lighter than the acid, and mingling with it: and that this could not be water diluting the acid, was evident from the specific gravity of the lighter portion being less than that of water itself. On submitting this to distillation, it became still lighter; and on neutralizing the acid existing in it by potash, and distilling the super-natant liquor, poured off from the acetate of potash, a liquor was obtained lighter than alkohol, volatile, highly inflammable,

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* Nicholson's Journal, vol. xiii. p. 42.

not sensibly acid, and miscible with water in all proportions. This etherial liquid, he adds, might be called Pyro-acetic ether, to distinguish it from real acetic ether, from which it differs entirely. It is it which diminishes the specific gravity of the latter portions of radical vinegar, and which probably also gives the acid in this state inflammability, and perhaps its volatility and penetrating smell; and Courtenvaux had before remarked, what is conformable to this, that it is the last portion that distils over in decomposing acetate of copper by heat that is inflammable and pungent. This product cannot be supposed to originate from any alkohol retained in combination with the acid in the acetate, but is probably formed from the reaction of the metallic oxide on the acetic acid, this taking place principally at the end of the process, when the greater part of the water has been expelled, and the temperature is raised high *. The same substance was examined by Chenevix, who gave it the name of Pyro-acetic Spirit. It is formed, he found, in the distillation of other metallic acetates, acetate of lead, zinc, or manganese, and in larger quantity, as the metal is less easily reduced to the metallic state. It is also obtained in the distillation of alkaline and earthy acetates. Heat alone does not convert acetic acid into the pyro-acetic spirit. It is decomposed by sulphuric, nitric, and muriatic acids, but affords no acetic ether †.

Acetic acid, in its highest state of concentration, such as that obtained from acetate of copper by heat, or distilled repeatedly from muriate of lime, has a fragrant and very penetrating smell: it is so caustic as to inflame the skin; its acid taste is strong, even when it is largely diluted with water: it is colourless, and has a specific gravity of 1.0626: from the intermixture, however, of the product just no-

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* Annales de Chimie, tom. lxiii.

† Nicholson's Journal, vol. xxvi. p. 225.

ticed, its strength cannot be judged of from its specific gravity. In its diluted state, as in that of distilled vinegar, its smell is more faint, but is still agreeable.

This acid is capable of congelation; it forms foliated arborescent crystals; and, according to the observations of Lowitz, it suffers this change, and presents very different results, according to its degree of concentration. If much diluted, as in common distilled vinegar, it is the water that freezes, leaving a stronger acid uncongealed; if the acid exposed to cold be more concentrated, it congeals, and the part remaining liquid is more watery. When strong, it congeals, according to his account, at 32°, and remains solid even at a higher temperature *. With regard to this, however, there is some obscurity; for concentrated acetic acid does not freeze at a much lower temperature, and the acid distilled from charcoal, Lowitz himself remarks, requires a temperature lower than 20° of Fahrenheit. The congelation is probably influenced by the intermixture of pyro-acetic spirit.

Acetic acid is very volatile: its odour is diffused through the atmosphere, and becomes gradually weaker; and, by a moderate heat, it is converted into vapour; this vapour catches fire on the approach of an ignited body; hence the acetic acid affords an example of an acid retaining inflammability. It appears, however, from the facts already stated, that this inflammability, and perhaps the volatility and pungency of odour, are in part owing to the presence of pyro-acetic spirit.

Acetic acid combines with the alkaline and earthy bases. Its salts are named Acetates, or formerly Acetites. They are very soluble in water, and the greater number of them are deliquescent, and not easily crystallized: the acetic acid is easily disengaged; and they are decomposed by heat,

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* { Annales de Chimie, tom. x. p. 215.
{ Crell's Chemical Journal, vol. i. 245. 252.

the greater part of the acid suffering decomposition, and leaving a residuum of charcoal.

ACETATE OF POTASH is prepared by saturating the alkali of carbonate of potash, by the addition of distilled vinegar. The liquor is evaporated to a dry mass: this is of a brownish colour, from the presence of a little extractive matter derived from the vinegar. If it be melted and kept in liquefaction for a short time, on dissolving it again in water, the extractive matter separates in flakes; the solution is limpid, and affords a salt perfectly white. It is soft and of a foliated texture, whence it received the name of Terra Foliata Tartari. Its concentrated solution affords, when exposed to cold, prismatic crystals. This salt is so deliquescent, that, on a few minutes exposure to the atmosphere, its surface becomes humid: it does not require more than its weight of water for its solution at 60°: it is also soluble in alkohol. Its watery solution, like that of other acetates, decomposes spontaneously. When the dry salt is exposed to heat, its acid is decomposed, an empyreumatic oil and acid pass over, with carbonic acid and carburetted hydrogen gases; a considerable quantity of charcoal remaining, with carbonate of potash.

ACETATE OF SODA crystallizes, when its solution is evaporated until a pellicle form on its surface, in striated prisms. Its taste is sharp and bitter: it is said on some authorities to be slightly deliquescent, on others not so, when perfectly pure; it is easily soluble in water, requiring only three parts at 60°. It is also soluble in alkohol.

ACETATE OF AMMONIA, formed by saturating carbonate of ammonia with distilled vinegar, has been known under the name of Spirit of Mindererus, having been employed in medicine as a diaphoretic. It is so volatile that its solution cannot be concentrated by hasty evaporation: by slow evaporation it may be obtained in acicular prisms; and it can be crystallized by sublimation. It is very deliquescent and soluble.

The compounds of acetic acid with the earths are not of much importance. Acetate of barytes crystallizes in acicular prisms, which are efflorescent, and very soluble in water. Its taste is bitter. Acetate of strontites affords, by evaporation, slender crystals, which are soluble in water, requiring not much more than two parts for their solution, and which are not altered by exposure to the air. Acetate of lime is obtained by evaporation and cooling, in fine prismatic crystals of a silky lustre, efflorescent, soluble in water, and still more soluble in alkohol. It consists, according to Berzelius, of acetic acid 64.6, lime 35.4. Acetate of magnesia crystallizes, but with difficulty, its solution affording, on evaporation, a viscid deliquescent mass, abundantly soluble both in water and alkohol: its taste is sweetish. Acetate of alumina, prepared by digesting the acid on the earth, forms small needle-like crystals, soft, and having an astringent taste. A singular property of this salt, noticed by Gay Lussac*, is that of its solution becoming turbid when heated, and recovering transparency when it cools. The precipitation is owing to the separation of a part of the alumina; and this, according to the explanation given by this chemist, depends on the heat separating the particles of the earth and acid beyond the sphere of their mutual attraction: The fact requires to be attended to in the preparation and application of this salt as a mordant in calico-printing. Acetate of glucine is formed by direct combination: the solution does not crystallize, but is reduced, by evaporation, to a gummy-like substance, which remains long ductile, and dries slowly: its taste is sweet and astringent. Acetate of zircon is likewise gelatinous and uncrystallizeable, and has an astringent taste. Acetate of ittria crystallizes in thin plates.

Acetic acid acts more or less powerfully on the metals, and, in general, combines with facility with them when they are oxidated. Some of these combinations, particularly those with lead and copper, are extensively used.

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* Nicholson's Journal, vol. xxxi. p. 33.

Gold, silver, and platina, are not affected by it in their metallic state, but their oxides are dissolved by it. The acetate of silver crystallizes in prisms, which are very soluble, and have a sharp metallic taste. Acetate of quicksilver is different in its properties, according to the state of oxidation of the metal. That in a low degree of oxidation is obtained by decomposing a solution of nitrate of quicksilver, in which the metal is in that state, by adding a solution in tepid water of acetate of potash : delicate crystals, in the form of spangles, of a white colour and silvery lustre, form quickly, and are deposited as the solution cools. Its principles have so weak an affinity, that it is decomposed by water : if a large quantity be employed to wash it, it becomes yellow : the whiteness is restored by washing with a little distilled vinegar : when dry, it forms a soft foliated mass : its taste is mild, but metallic. The acetate formed by digesting the acid on mercury more highly oxidated, as on the red oxide, is more acrid and soluble.

Copper forms with acetic acid combinations of some importance, from their use in medicine and the arts. What is named Verdigris is a sub-acetate of copper. It is prepared by stratifying copper plates with the husks of the grape, brought into fermentation by having been kept in a warm apartment, with some degree of moisture. The copper plates are placed in layers, with the husks thus prepared, in jars, which are covered. At the end of fifteen or twenty days, these are opened : the plates have an efflorescence on their surface of a green colour : they are repeatedly moistened with water ; and a length a crust is formed, which is scraped off, is put into bags, and dried by exposure to the air and sun. It is of a green colour, with a slight tint of blue *. In this preparation, the copper is oxidated, probably by the atmospheric air, aided by the affinity of the acetic acid produced by the fermentation: and a portion of this acid remains in combination with the oxide, not sufficient, however, to produce its saturation. When it is acted on, therefore, by water, a portion of oxide remains undissolved; and from this mode of analysis Proust inferred, that it consists of 43 of acetate of copper, 27 of black oxide of copper, and 30 of water, this water existing in it in intimate combination †. A specimen of verdigris, manufactured in England, was found by Dr Thomson to consist of soluble matter 45.7, composed of 32.85 of acetate of copper, and 12.85 of water, with insoluble matter, composed of sub-acetate of copper 23.36, carbonate of copper 12.10, water 18.84 ‡.

The proper acetate of copper is prepared by dissolving verdigris in distilled vinegar: the solution, when evaporated, affords masses composed of prismatic crystals, aggregated, of a deep green colour, but which becomes lighter from efflorescence on exposure to the air. This salt is soluble in water, and in alkohol: it has a strong metallic taste. It consists, according to Proust, of 39 of oxide, and 61 of acid and water. Both it and verdigris are used as pigments, in some of the processes of dyeing, and in medicine from their escharotic power.

With lead, acetic acid forms combinations of some importance. Cerusse, or white lead, is formed by exposing plates of lead to the vapours arising from boiling vinegar; the metal is oxidated by the action of the air, aided by the affinity of the acid, and a crust is formed, which is scraped off and levigated. This has been regarded either as an

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* Account of the Manufacture of Verdigris, by Chaptal, Philosophical Magazine, vol. iv. p. 71.

† Journal de Physique, tom. lxi. p. 114.

‡ Annals of Philosophy, vol. vii. p. 401.

oxide or a sub-carbonate of lead. By farther combination with acetic acid, a salt is obtained in a crystalline form, named from its sweetness Sugar of Lead. To prepare it, cerusse, in fine powder, is boiled in distilled vinegar, the vinegar being poured off as it loses its acidity, and fresh quantities being successively added; the liquors thus procured are evaporated nearly to the consistence of honey; and, on cooling, masses are formed, consisting of a congeries of needle-like prisms. According to the account given by Pontier of the manufacture of this salt, it is also formed by exposing plates of lead to the action of distilled vinegar and of the atmospheric air: the plates, as they are incrusted with oxide at the surface of the vinegar, are plunged to the bottom, until this oxide is dissolved, and are again raised to the surface. The acid is thus saturated, and, by evaporation, the solution is brought to crystallize*.

This salt was regarded as the neutral acetate of lead. From the researches of Thenard it appears, that it contains an excess of acid, which modifies its properties. It sometimes happens in preparing it, that it does not crystallize in the usual form, but in plates; Thenard examined this product, and found it to be the neutral acetate, while the common sugar of lead is always a super-acetate. The latter, he found, consists of oxide of lead 58, acetic acid 26, and water 16†. The form of its crystals is a slender four or six sided prism bevelled at the extremities; its colour is white, or frequently of a yellowish tinge, with a silky lustre; its taste is sweet and styptic; it is slightly efflorescent; is easily soluble in water, requiring not more than 3 parts at 60° for its solution; by the addition of a large quantity of water, it appears to be partially decomposed, as the solution, even with distilled water, is milky; a small quantity of a white powder is deposited, and the salt which remains dissolved, has probably a greater excess of acid than the original salt. It is decomposed by all those salts which contain an acid that forms an insoluble compound with oxide of lead, and is sometimes used as a test to discover their presence. It is also decomposed by heat, and gives empyreumatic acetic acid.

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* Annales de Chimie, tom. xxxvii. p. 268.

† Nicholson's Journal, vol. vi. p. 225.

The neutral acetate formed by boiling the super-acetate with oxide of lead, is described by Thenard as crystallizing in plates; its taste is less saccharine than that of the super-acetate; it effloresces slightly; is less soluble in water, and forms a solution which is precipitated abundantly by carbonic acid, while that of the super-acetate is precipitated sparingly. It dissolves in vinegar, and on evaporation gives needle-like crystals. It consists, according to his analysis, of oxide of lead 78, acetic acid 17, water 5. What is named Goulard's Extract, prepared by boiling vinegar on litharge until it is saturated with it, is, according to Dr Bostock's experiments, a solution of neutral acetate of lead. According to Berzelius, the super-acetate, or acetate as he names it, rendered as dry as possible, consists of oxide of lead 58.71, acetic acid 26.97, water 14.32. The other salt, the soluble acetate, or sub-acetate as he names it, can be obtained by exposure in a vacuum with sulphuric acid, perfectly dry; it then consists of 86.77 oxide of lead, and 13.23 of acetic acid. The quantity of acid in the one salt is three times that contained in the other[*].

Acetic acid dissolves iron, the metal being oxidated by the water. The solution is of a reddish brown colour; has a sweetish astringent taste; and by evaporation affords a gelatinous mass, which is deliquescent and easily decomposed by heat. The use of this solution as a mordant in calico-printing, has been already mentioned.

The remaining metallic acetates present few important results. The acid dissolves tin in small quantity: the solution when evaporated is viscid, and has a fœtid smell. Zinc is dissolved by it readily, and by evaporation crystals in thin plates are obtained, which burn, when thrown on ignited fuel, with a blue flame, and are decomposed by heat. Nickel is dissolved by acetic acid, and the solution, by evaporation, gives crystals of a green colour. Oxide of cobalt is dissolved by it; the solution is of a pale rose colour, and forms a sympathetic ink. Antimony and bismuth are scarcely affected by it: the vitrified oxide of antimony appears to be dissolved in small quantity. Oxide of arsenic is said not to combine directly with it; but when heated with acetate of potash, a liquor is formed, fuming and having a very fœtid odour, which the Dijon Academicians found inflamed spontaneously on exposure to the air, and exhaled a dense fœtid vapour. The residuum of the decomposition of all the metallic acetates by heat contains charcoal in such a state, that they are in general pyrophoric, and several of them readily take fire on exposure to the air.

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[*] Annals of Philosophy, vol. v. p. 175.

Acetic acid acts on several of the vegetable products. Hatchet found that it dissolves resins and gum-resins, without altering their properties. It also dissolves gluten, camphor, and essential oils. It combines with alkohol, and when its action is promoted by heat, converts it into a species of ether, which has been already noticed.

This acid affords the usual products of the vegetable acids when decomposed by heat, and therefore contains carbon, hydrogen, and oxygen. Lavoisier had obtained ammonia in its decomposition, and Proust prussic acid *, whence it might be inferred to contain nitrogen; but Trommsdorff observed, that it affords neither of these when the acid is pure. Gay Lussac and Thenard give as its composition, from their usual mode of analysis, carbon

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* Journal de Physique, tom. lvi. p. 105.

50.224, oxygen 44.147, hydrogen 5.629. Berzelius has assigned as the proportions, carbon 46.83, oxygen 46.82, hydrogen 6.35 *. But in these, as in all the analogous cases, he infers the composition of the acid abstracted from what he considers as its combined water. Estimating the quantity of this from the oxygen in the quantity of base which the acid saturates, it amounts to 17.56, or 15.56 of oxygen and 2 of hydrogen. And adding these to the above proportions, we have as the composition, carbon 46.83, oxygen 62.4, hydrogen 8.35. This is very nearly the second definite proportion of oxygen to carbon, and also the second proportion of hydrogen. Acetic acid, therefore, is represented by carbonic oxide, with hydrogen in the proportion which constitutes super-carburetted hydrogen.

Acetic acid, in its various states of dilution and purity, is applied to numerous uses. Vinegar is one of the acids that has been longest known, and is extensively used as a condiment and an antiseptic. It is employed in medicinal practice, and in a number of the processes of pharmacy. And its saline and metallic combinations are used in several of the arts.

SECT. III.—OF THE PUTREFACTIVE FERMENTATION.

PUTREFACTION is a process to which animal matter is more peculiarly liable. Some vegetable substances, however, likewise undergo it; and if others, in the ultimate spontaneous decomposition to which they are liable, do not give out those offensive products which characterize the putrefaction of animal matter, they so far present si-

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* Annals of Philosophy, vol. v. p. 176.

milar results, that their composition appears to be completely destroyed; their principles enter into new combinations, which escape in the aërial form; and they leave nothing but the small quantity of earthy and metallic matter, which the vegetable substance had contained. As this change follows the acetous, and has been supposed to be in general preceded by it, it has been considered as the last of the three stages of the process of fermentation, and has been distinguished by the epithet Putrefactive.

Every kind of vegetable matter nearly is liable to this species of decomposition. Those suffer it most quickly which are soluble in water; and any vegetable principle dissolved in this fluid, passes speedily into it: the surface of the liquor appears covered with a mould; elastic fluids are disengaged, and at length it is entirely decomposed. Those which are not perfectly soluble, if kept humid, present nearly the same results. Oils and resins, which refuse to unite with water or imbibe it, resist any change of this kind for a long period, and can indeed scarcely be said to be subject to it.

The same circumstances favour this species of spontaneous decomposition, which favour the others, particularly humidity, and a moderate heat. Any vegetable matter, kept perfectly dry, is long in exhibiting any sign of alteration or decay. A certain temperature, which must be less, however, than what will dissipate the humidity, hastens the decomposition, by favouring the approximation, and consequent exertion of the affinities of the constituent elements. And the presence of the air often promotes it; at the same time, however, modifying the results.

The gases disengaged during this decomposition arise from combinations of the principles of the vegetable substance. According to Saussure, they are compounds of hydrogen with carbon, and carbonic acid. The former appear principally when the atmosphere is excluded, by the substance being immersed under water: the latter when the air is admitted, and its production depends in a great measure on the action of the oxygen of the atmosphere *. A portion of water is also formed, by the union of part of the oxygen and hydrogen of the vegetable matter.

The principal difference between this species of decomposition, and the putrefaction of animal matter, is, that there is no evolution of ammonia, or of those fœtid combinations which characterize the latter. This is owing to the absence of nitrogen, which is essential to the formation of these. And accordingly, those varieties of vegetable matter which contain this element, present, in their ultimate decomposition, results similar to those of animal substances: such is particularly the case with those which contain gluten, and with gluten itself in its pure form.

The residual matter of vegetable substances, after this decomposition, frequently contains a large proportion of carbon, especially when formed from those principles in which this element is abundant, as from the ligneous fibre; and this may remain long unaltered, the other principles which re-act upon it having been abstracted in the progress of the decomposition. A residuum of this kind forms that black soft matter named Vegetable Mould, which constitutes so important a part of the soil.

When this is obtained free from the undecomposed vegetable matter mixed with it, it appears from the researches of Saussure †, to be nearly uniform in composition and properties. Subjected to distillation, it yields carburetted hydrogen, and carbonic acid gases, water holding in solution acetate and sometimes carbonate of ammonia, and a small quantity of empyreumatic oil, leaving charcoal, with saline and earthy ingredients. From these products it follows, that the mould contains less oxygen, more carbon and more nitrogen, than the vegetable matter from which

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* Recherches Chimiques, p. 157.

† Ibid. p. 162.

it has been formed; though part of this nitrogen probably is derived from the animal matter unavoidably mixed with it.

The acids do not exert any striking action on this mould; they dissolve its earthy and metallic ingredients. The fixed alkalis dissolve it, and evolve ammonia during the solution. Alkohol takes up a little resino-extractive matter. Water dissolves a small quantity of extract.

Saussure has remarked, that vegetable mould, though the result of the putrefactive process, is not itself susceptible of putrefaction, but even retards it; hence it remains unaltered, evidently from the cause already assigned, that no other principles are present in sufficient proportion to act on the carbon accumulated in it. This, however, is only when the air is excluded; when exposed to the atmosphere, it suffers a gradual change, until it is entirely decomposed. The oxygen of the air combines with its carbon, forming carbonic acid, as Saussure found by inclosing it over quicksilver in atmospheric air or oxygen gas. While this proceeds, the abstraction of carbon appears to allow part of the oxygen and hydrogen of the mould to combine and form water; for it loses more of its weight than can be accounted for from the quantity of carbon abstracted. These changes proceed in a certain relation to each other, and terminate at length in the entire decomposition, leaving the earthy and metallic substances originally contained in the vegetable matter. We perceive from this view, how necessary the frequent turning up of the soil is, to enable vegetable mould to form a proper manure, by decomposing, and affording carbonic acid to the growing plant. And we discover also the cause of the inertness and unfertility of that accumulation of it, which principally constitutes peat and morass, and which, if it is not subjected to such operations, remains for ages unchanged.

When the slow and spontaneous decomposition of vegetable substances is conducted under peculiar circumstances, the result is the accumulation of carbon in the residual matter; and beyond this the decomposition frequently does not proceed. The circumstances on which this is dependent, are not, perhaps, perfectly determined; but they seem to be, principally, a due humidity, a certain degree of compression, and the exclusion of atmospheric air. These are all present when the substance is buried to some depth in the earth, and although in this situation the process must proceed very slowly, still there is reason to believe that this species of spontaneous decomposition takes place.

We can perceive, so far at least, how these circumstances operate in giving rise to this peculiar result. A certain degree of humidity is requisite to favour the mutual actions of the principles of the vegetable matter. Were the atmosphere freely admitted, its oxygen would modify these actions, and, in particular, by its affinity to carbon, would abstract the greater part, and allow the remaining principles to enter into other combinations: its exclusion, therefore, both checks the progress of the decomposition, and favours the accumulation of carbon. Compression seems to operate by opposing the formation of elastic compounds: were it not present, it is probable, that, in the re-action of the elements of the vegetable matter, the oxygen would combine partly with hydrogen, and form water, and partly with carbon, and form carbonic acid. But compression opposing an obstacle to the formation of the latter substance, the combination of oxygen with hydrogen is determined, and thus carbon is predominant in the residual matter.

It is obvious, also, that those kinds of vegetable matter which contain the largest proportion of carbon will exhibit most completely this result. Hence it is conspicuous in wood.

On these principles, I conceive, may be explained this species of decomposition, the existence of which cannot be doubted, since we perceive it particularly exemplified in wood that has been kept humid, and buried to a certain depth. And the various coally and bituminous substances which are found in the earth have been probably formed by some such process. Their origin from vegetables is clearly marked in their composition and properties: they are inflammable; afford, by destructive distillation or combustion, the usual products of vegetable matter; the remains of vegetable and animal substances are often intermixed with them, and we can even trace the gradation from wood slightly changed to those which are most remote from the ligneous texture. These Bitumens have been already considered.

BOOK IX.

OF ANIMAL SUBSTANCES.

THE chemical history of Animal, like that of Vegetable Substances, may be comprised under three divisions. In the first may be considered, what relates to their general chemical constitution, and to their formation, so far as this is dependent on chemical action. Under the second may be described, the varieties of animal matter; their distinctive characters, chemical properties, and combinations: And their history may be concluded, with an account of the spontaneous changes to which they are liable, and the decompositions they suffer from the re-action of their constituent elements, either at high or at low temperatures.

CHAP. I.

OF THE FORMATION OF ANIMAL SUBSTANCES.

Animal, like vegetable substances, are formed of a few simple principles; the differences in their properties arising from variations in the proportions, and in the modes in which these are combined. They are still more susceptible of decomposition; the balance of affinities whence they exist, being altered by very slight causes, and their elements easily entering into new combinations.

There are certain chemical characters by which the animal are distinguished from the vegetable products. They are more liable to that species of spontaneous decomposition named Putrefaction. Vegetables in a humid state, either pass into the vinous or acetous fermentation, or suffer that species of decomposition whence carbonic acid and carburetted hydrogen gases are disengaged, and charcoal remains. Animal substances are liable to none of these changes, or at least are little disposed to pass into them; they rather undergo the putrefactive fermentation, that is, their elements enter into combinations, the principal of which are ammonia, and certain elastic fluids more compound than those formed in the decomposition of vegetable matter.

When vegetables are decomposed by heat, the products of the decomposition are empyreumatic oil and acid, carburetted hydrogen, carbonic oxide, and carbonic acid gases, the residuum being charcoal. Some afford ammonia, but it is yielded only in small quantity, and by a few of them. Animal substances, with the usual products of the analysis of vegetable matter, invariably afford a large quantity of ammonia when they are decomposed by heat. They give also some other peculiar products, particularly compounds of sulphur and phosphorus with hydrogen, the prussic acid, and phosphoric salts.

These differences arise from the difference in their chemical composition. That of animal substances is more complicated than that of vegetable matter; besides carbon, hydrogen, and oxygen, they always contain nitrogen, and generally phosphorus and sulphur. The presence of these dividing the attractions subsisting between the carbon, hydrogen, and oxygen, weakens their force, and hence these complicated compounds are more liable to decomposition, and their elements have a powerful tendency to enter into binary or ternary combinations. To this is owing the great susceptibility of decomposition which characterizes the animal products.

The peculiar products they afford by their analysis, derive their origin from those elements which are more peculiar to them. The nitrogen, which may be considered as the principle that gives them their character, by combining with hydrogen, furnishes the ammonia, which is evolved during their putrefaction and their decomposition by heat: it forms a principal component part of the prussic acid, and it enters into the composition of the gases they give out.

Phosphorus is another element present in the greater number of the animal substances, and nearly peculiar to them. During their decomposition it enters into new combinations, particularly with hydrogen and nitrogen, and forms those compound gases which are disengaged. When they are decomposed by the action of nitric acid, it is converted into phosphoric acid, and remains mixed, as Berthollet shewed *, with the oxalic acid usually formed in that process. On its presence also depends the abun-

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* Mémoires de l'Acad. des Sciences, 1785, p. 548.

dance of salts formed by the union of phosphoric acid with the earths, and alkalis, which are so generally afforded by their analysis.

Sulphur is likewise a component part of several animal substances; it enters into the composition of the products of their decomposition, particularly of the elastic fluids which are extricated.

It may be added as another general difference in composition between animal and vegetable substances, that the former contain less carbon and more hydrogen than the latter. Carbon appears to be the base of vegetable matter, to which oxygen and hydrogen are attached. Hydrogen seems to be the principal component part of animal matter combined with nitrogen, oxygen, carbon, and phosphorus. Hence, in the decomposition of animal substances, much empyreumatic oil is obtained, of which hydrogen is the chief constituent, while another portion of it is spent in the formation of ammonia. In general, the animal substances contain less oxygen than the vegetable, and therefore afford less acid in their decomposition.

In entering on the investigation of the formation of the animal products, it may be stated as a fundamental proposition, that they are derived from changes effected in the animal system on vegetable matter. All animals live directly or indirectly on vegetables, and derive from them almost their sole support. This leads to the consideration of Digestion, Respiration, and Secretion, the three functions which compose, by their union, the process of animalization. Though these functions are in some measure regulated by laws peculiar to the living system, these do not suspend the exertion of the usual laws to which the matter concerned in them is subject. Affinities are exerted between the particles of that matter, and new combinations are established; and it belongs to chemistry to trace these combinations, and the circumstances by which they are modified, and thus to elucidate the phenomena of physiology connected with these actions.

An important distinction exists between animals and vegetables, in the mode in which they receive nourishment. Vegetables are constantly absorbing matter from the soil: it passes into the general sap-vessels, and is soon changed by respiration and secretion. Animals, with few exceptions, take in food at intervals, and retain it in their stomach until it undergoes a chemical change. It is this which constitutes the function of digestion, the first step in the general process by which animal matter is formed.

In the process of digestion, the food is subjected to a temperature usually above 90 of Fahrenheit; it is mixed with the gastric juice, a liquor secreted by the glands of the stomach; and it undergoes a moderate and alternate pressure, by the contraction of the stomach itself. It is thus converted into a soft uniform mass of a greyish colour, in which the previous texture, or nature of the aliment, can be no longer distinguished.

In the production of these changes, the gastric fluid appears to be the principal agent. It has been proved by the experiments of Stevens, Spallanzani, and others, that it possesses a real solvent power, or that, independent of heat or pressure, and even out of the body, it is capable of dissolving animal and vegetable matter. At the same time, these circumstances promote its action, and are therefore assistant causes in the process of digestion. In the graniverous animals, trituration, from the action of the stomach, has a very important share in reducing the food to that state in which it is more easily acted on; while in carniverous animals, which have a membranous stomach, the effect is produced almost entirely by the action of the gastric fluid.

The nature of the change which the food suffers in the stomach, has not been well ascertained. It does not seem to be resolved into its ultimate principles, from which new combinations are formed. The soluble parts of the vegetable and animal matter, the mucilage, fecula, sugar, and oil of the one, the gelatin, albumen, and other principles of the other, are rather separated from the insoluble parts of each, and brought into a state of intimate mixture with each other, so as to be more readily acted on by the other chemical powers to which it is to be exposed. It is at the same time partially animalized by the mixture of the saliva and gastric fluid, by which probably its further assimilation is facilitated.

The Chyme, as the pulpy mass into which the food in the stomach is resolved, is termed, passes by the pylorus into the intestinal canal, where it is mixed with the pancreatic fluid and the bile, and is still exposed to the same temperature and alternating pressure. The thinner parts of it are absorbed by the slender tubes termed the Lacteals: the liquor thus absorbed is of a white colour: it passes through the glands of the mesentery, and is at length conveyed by the thoracic duct into the blood.

This part of the process is termed Chylification, and the white liquor is the Chyle. It is an opaque milky fluid, mild to the taste. By standing for some time, one part of it coagulates; another portion is coagulated by heat.

We know little of the nature of the changes which constitute Chylification. Some have supposed that the bile, or some part of it, combines with part of the food, and animalizes it; while others suppose bile to be an excrementitious fluid, useful only in stimulating the intestines to action. Neither opinion has been proved, though the former seems more probable than the latter, from the large quantity of bile secreted, compared with the quantity discharged from the intestines. We know still less of the changes which the chyle suffers in its passage through the mesenteric glands; but by the general process it is assimilated to the nature of animal matter, as it possesses the property of albumen, of being coagulated by heat.

The chyle, after mixing with the lymph conveyed by the absorbent vessels, is received into the blood which has returned from the extreme vessels, and before it passes to the heart. All traces of it are soon lost in the blood, as it mixes perfectly with that fluid. It is probable, however, that its nature is not immediately completely altered. The blood passing from the heart is conveyed to the lungs, where it circulates over a very extensive surface presented to the atmospheric air, with the intervention of a thin membrane, which does not prevent their mutual action. During this circulation, it loses a considerable quantity of carbon, part of which, it is probable, is derived from the imperfectly assimilated chyle, as this, originating in part from vegetable matter, must contain carbon in larger proportion than the blood itself.

The process of sanguification is probably not completed even with this change. The blood returning to the heart, is distributed over the whole body. In the extreme vessels it is converted from the arterial to the venous state, and though this is connected with the different species of secretion, it is probable also, that in these vessels the process of animalization is finished. There remains, as the result of it, a redundance of carbon; and the venous blood is brought back to the heart, and conveyed to the lungs, where this excess of carbon is discharged.

If we examine the composition of the blood, we find it to be entirely different from that of vegetable matter, from which it is ultimately derived. It is a heterogeneous fluid, composed of various principles, which all possess the general characters of animal matter.

From this fluid the solids seem to derive their nourishment, by attracting immediately the principles which it contains ready formed; for there is perhaps no solid in the animal body, of which not merely the ultimate, but even the immediate principles exist in the blood.

There is another process, however, that of Secretion, by which new products are formed. In the course of the circulation, the blood is conveyed to certain organs named Glands, and is there changed in composition, so as to form various products not pre-existing in the mass of blood; and which form some of the most important varieties of animal matter.

Various hypotheses have been given of the nature of secretion. At one time it was regarded as mechanical,—as a species of filtration; but the fact, that the products are different from any existing in the blood, affords a sufficient refutation of this opinion, and proves it to be chemical. A fluid is received into vessels, in its progress through which its composition is changed, not merely from the abstraction of principles previously existing in it, but from new combinations of its elements. From the description of this process, it is evident that it consists of a series of chemical actions. But if we endeavour to investigate how these are effected, or inquire by what powers these new chemical compounds are formed, we scarcely can propose any satisfactory theory. In the structure of the glands we perceive nothing but a series of convoluted vessels, through which the blood circulates, and we are unable to discover how the action of these vessels can operate so as to form one new product; far less, how different glands can, from the same fluid, form substances entirely different in chemical composition and properties.

On a subject so obscure, it is impossible to give more than hypothesis, which can scarcely be supported by direct proof. Yet if it afford any probable explanation of the phenomena, it is so far satisfactory. The cause productive of the new combinations which constitute secretion, may be the simple approximation of the elements existing in the blood. That fluid is propelled by a *vis à tergo* into canals of extreme minuteness, the diameters of which are farther diminished, from their contraction from the stimulus of the blood. There can be no doubt, that, in compounds, the force of attraction subsisting between their constituent particles is modified by the distances at which these are placed; and in compounds especially which consist of four or more principles, the slightest alteration in their relative situation is sufficient to change the existing attractions, and induce new combinations. The blood is a compound of this kind: its ultimate principles, too, are capable of entering into an innumerable variety of combinations with each other. We may conceive, therefore, that, when subjected to the contraction of the minute vessels through which it is forced to circulate, the relative positions of its elements may be changed, their attractions will thus be altered, and new combinations formed. And if we suppose a fluid thus passing through tubes of different diameters, and undergoing successive decompositions, we may easily conceive, that very different products may be formed from the same original compound.

This affords a simple view of the nature of secretion. No complicated apparatus is requisite for the performance of the change, all that is necessary being the propulsion of the blood through minute vessels, capable of contraction. It has accordingly frequently been observed, that new products are formed without the intervention of glands; such is the formation of the fat, or of the muscular fibre. It is easy to conceive, that the formation of these may take place in the extreme vessels, where these products are deposited; and, in like manner, in the mere course of the circulation, may be formed the gluten, albumen, and other principles of the blood itself.

From secretion a variety of products are formed, as the bile, milk, fat, the bony matter, the matter of membranes, and a variety of others. These complete the formation of animal matter, and comprehend its several varieties.

Such are the different steps of the process of animalization. The food is digested in the stomach, mixed with animal matter in the intestinal canal, and converted into chyle: this mingles with the blood, and loses a portion of carbon in the lungs: in the extreme vessels it is converted into the general principles of animal matter; and, in the glands, is converted into various secreted products.

Since animal substances are thus formed by the processes of digestion and respiration, it becomes an object of inquiry, whether, from the principles known to be conveyed by these processes, we can explain their formation. Their ultimate elements are carbon, hydrogen, oxygen, nitrogen, sulphur, and phosphorus, with smaller portions of lime, iron, potash, and soda. Are these, or any of them, formed by the animal system, or are they merely introduced into the body from without, and brought into new combinations? This question cannot perhaps be satisfactorily determined while we know so little of the real elements of bodies. Yet it is so far interesting to trace their origin where this can be done.

With regard to carbon, hydrogen, and oxygen, there is no difficulty. They exist in vegetable matter in a proportion even larger than that in which they exist in the animal products, and it is evident, therefore, that they are conveyed by the food.

To trace the origin of the nitrogen in the animal system is much more difficult. There is no question, indeed, relating to animal chemistry, involved in so much obscurity as this, when we consider the large quantity of nitrogen that is contained in almost every variety of animal matter. It exists in small quantity in vegetable matter, and only in some varieties of it; and as many animals live entirely on vegetable food, and almost all may be brought to live principally on it, it seems evident, that it cannot be derived from this source. It has been supposed to be received in respiration. Priestley, Goodwin, Davy, and other chemists, found reason to conclude, from experiments afterwards to be stated, that there is a consumption of nitrogen in this process to a certain extent; and this would afford a source whence all the nitrogen found in the animal system may be derived. But the fact, as is afterwards to be stated, is doubtful; and it is difficult indeed to conceive of any mode in which the consumption of nitrogen should be connected in the action of the air on the blood, with the consumption of oxygen. Though nitrogen may not, however, be consumed, properly speaking, in the chemical process of respiration, there is a mode in which I conceive it not improbable that it may be conveyed into the blood from the lungs. The residual air which occupies the air-cells after expiration, is chiefly nitrogen, or at least, it contains it in much larger proportion than even the large proportion in atmospheric air. An air of this kind constantly remaining in the bronchiæ, and being applied to the moist surface of the membrane forming the minute blood-vessels, a portion of it condensed by the humidity of that membrane may permeate it, and be absorbed into the mass of blood. This effect may be altogether unconnected with the chemical changes of the air in respiration, and may proceed so slowly as not to be discoverable with precision by any change in the inspired air, while at the same time acting constantly, it may be sufficient to afford the whole of this element which is necessary to the formation of animal matter. A diminution in the volume of the air in respiration has even been very generally observed in the experiments on this subject, which would be conformable to this result. This has been supposed to arise from the changes connected with the action of the oxygen of the air on the blood, while it may arise from this abstraction of nitrogen. In some of the experiments, accordingly, a loss of nitrogen appeared to be proved: while in others, conducted perhaps with more accuracy, this has not been observed. But as the result can only be determined with precision, so far as it affects the above explanation, by respiration continued for a considerable period, and as this cannot be conducted independent of the influence of voluntary exertion and other circumstances affecting the volume of air passed through the lungs, it is scarcely possible to establish the conclusion with perfect certainty; nor in the present state of experimental investigations can it be considered as established, so as to exclude the hypothesis I have stated. On the general question I may also add, however, that nitrogen may either be a compound, or may exist in the composition of others, which are ranked at present as elementary, and that its origin in the animal system may perhaps be connected with one or other of these conclusions.

Phosphorus is another substance which exists in sparing quantity in vegetables, and is contained more abundantly in animal matter. Its origin is not less obscure. Some have supposed, that it is a product of animalization; which appears not improbable, when we consider the proportion of phosphorus which exists in the solids that constitute the animal fabric, and the large quantity of phosphoric salts discharged as excrementitious. It appears, however, that a considerable proportion of it is contained in those varieties of vegetable matter which are chiefly subservient to animal nourishment. Vauquelin found it in the farina of wheat, constituting, probably, an element in the composition of the gluten: the ashes of one pound of wheaten flour yielded about 34 grains of phosphate of lime; whence he has calculated, that a person taking one pound of this flour daily, would, in the course of one year, receive 3 lbs. 6½ ounces of this salt. Many animals live on food in which the existence of this principle has not been established, those, for example, which feed on grass; but then it is to be remarked, what is favourable to the opinion that it is derived from the food, that the urine of these animals contains no phosphoric salts. An accurate analysis of the vegetable nutritious substances, with a comparison of the composition of the solids and fluids of the animals which feed upon them, are wanting to throw light on this subject.

Similar difficulties exist with regard to lime and iron, the two principal remaining substances which enter into the composition of animal matter. Both of them are found in almost all the vegetable products; and lime is contained in every kind of water which can be used by animals as drink. Yet facts have also been stated, in proof that they are formed in the process of animalization. Thus Vauquelin, from the analysis of the egg of a hen, compared with the food which the animal received, found reason to conclude, that the quantity of phosphate and of carbonate of lime discharged was greater than what was contained in the food *; whence it followed, that both lime and phosphorus had been generated in the animal system. Other facts which have been stated are less conclusive: the argument drawn from the large quantity of calcareous matter secreted by certain marine animals, to form their shells, is evidently so, as a quantity of lime in a state of combination exists in sea-water. And the experiments which have been stated to prove, that an egg, previous to incubation, contains less lime and less iron than the chick does immediately after it is hatched †, are too inaccurate to admit of any certain conclusion. This remark applies, perhaps, to nearly all the researches on this subject. The general fact, that the greater part of those substances used as food by animals contain these principles, is perhaps sufficient to justify the belief, that they are introduced into the body, and not actually formed; any analysis by which the question might be determined with more precision being liable to such difficulties and sources of fallacy, that, as hitherto executed, it can afford no certain conclusion.

Few general chemical properties can be assigned as distinctive of animal substances. The principal one is their great susceptibility of decomposition, and their tendency

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* Annales de Chimie, tom. xxix. p. 22.

† Abernethy, Physiological Essays.

to pass into that species of decomposition which constitutes putrefaction, both of these arising from their complicated composition,—their elements being numerous, having their affinities more nicely adjusted, and being therefore more easily subverted; and these elements forming, when they enter into new combinations, those aeriform products, the evolution of which characterizes the putrefactive process. A number of the animal proximate principles have properties analogous to those of the vegetable principles. Animal mucus bears some resemblance to vegetable mucilage; animal fat has the characters of expressed vegetable oil; there are acids belonging to the animal as there are to the vegetable system, and some of these acids are common to both; saccharine matter is found in the animal as well as among the vegetable products; the gluten of vegetables is similar to the fibrin of animals; and in some animal products are principles analogous to extract, resin, and essential oil. There are, at the same time, principles peculiar to the animal system, as there are others confined to the vegetable kingdom.

The analysis of animal substances has been generally effected by the application of heat. Some information may also be derived from the action of re-agents. Thus, nitric acid expels nitrogen from several of them, and converts the residual matter into oxalic acid; and sulphuric acid chars them, or produces artificial tannin. According to Thenard, some animal substances combine with acids, as he supposes vegetable matter to do, and neutralize the acid powers: the caseous matter, albumen, picromel, gelatin, and urée, have this property.

Gay Lussac and Thenard applied the oxygenating operation of oxymuriate of potash to the analysis of animal, as well as that of vegetable matter. Greater precaution, however, is necessary in its application to animal substances; for, from the nitrogen which they contain, if too much oxymuriate be employed, a portion of nitrous acid is formed, which leads into error. This is obviated by avoiding an excess of oxymuriate, but employing as much as may be found, by preliminary trials, sufficient to convert the carbon of the animal matter, when heat is applied, into carbonic acid or carbonic oxide; and by thus subverting the combination of the elements, allow the hydrogen and nitrogen to pass into the gaseous state. By this method they analysed the four most important animal principles, fibrin, albumen, gelatin, and caseous matter *. The following table exhibits the results.

TABLE of the Analysis of the following Animal Principles, Fibrin, Albumen, Cheese, and Gelatin.

Substance analysed.	Carbon contained in it.	Oxygen contained in it.	Hydrog. contained in it.	Nitrogen contained in it.	Or supposing the oxygen and hydrogen to be in the state of water, and the nitrogen in the state of ammonia.			
					Carbon.	Water.	Ammonia.	Nitrogen in excess, or deficient.
Fibrin . .	53.360	19 865	7.021	19.934	53.360	22.369	23.463	+ 0 808
Albumen	52.883	23.872	7.540	15.705	52.883	27.127	23.182	—3.191
Cheese . .	59.781	11.409	7.429	21.381	59.781	12.964	31.778	—4.623
Gelatin . .	47.881	27.207	7.914	16.998	47.881	30.917	22.743	—1.541

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* Recherches Physico-Chimiques, t. ii. p. 324, 337.

With regard to all these proportions they give an excess of hydrogen above that which, with oxygen, forms water; and this excess of hydrogen, compared with the nitrogen they contain, is not far from the proportion in which these elements form ammonia. Under this point of view, they may be considered as composed of carbon, a certain quantity of oxygen and hydrogen in the proportions which form water, and a certain quantity of nitrogen and hydrogen in the proportions which form ammonia. By analogy from the law which, according to these chemists, exists with regard to vegetable substances, it may be inferred, that in the animal acids there is an excess of oxygen above these proportions, and in the animal fats an excess of hydrogen; this law, however, Gay Lussac has since admitted to be doubtful.

Berard has lately given the composition of some other animal principles. He employed for the purpose of analysis, the brown oxide of copper, heated with the animal matter, a method originally employed by Gay Lussac, and which has the advantages, that the oxide is easily reduced by the hydrogen and carbon, so as to form water and carbonic acid, allowing the nitrogen to be liberated; that it contains a large portion of oxygen, and this sufficiently condensed, so that it forms only a small portion of nitrous gas by its action on the animal matter; and that this nitrous gas can be decomposed so as to afford its nitrogen, by passing it over a layer of copper in filings heated, which at the same time has not the effect of decomposing the water or the carbonic acid.

To conduct the analysis, the animal substance is mixed with 20 or 25 times its weight of oxide of copper, and the mixture is put into a glass tube, nearly of the size of a barometer tube, and closed at one end. Over the mixture a layer of the oxide is put, to complete the decomposition of the substance, and its conversion into water and carbonic acid; and above this a layer of copper filings, to decompose any nitrous gas that may have been formed. The tube being placed so that the gaseous products can be collected, heat is applied, beginning at that part occupied by the copper filings: at an obscure red heat, the carbon of the animal matter combines with its oxygen, or with that of the oxide, and forms carbonic acid, the hydrogen forms water, and the nitrogen is disengaged in the gaseous form. The carbonic acid gas is obsorbed by a solution of potash; the oxygen furnished by the oxide of copper is known by the loss of weight which the latter sustains in the operation; and the water is estimated by calculation, or by the difference of the weight of the animal matter and the oxide of copper before the operation, to those of the nitrogen, carbonic acid, and the oxide after the same operation. The following table gives the proportions of the elements of the substances enumerated in it, by weight *.

In 100 parts of	Nitrogen.	Carbon.	Oxygen.	Hydrogen.
Ureè	43.40	19.40	26.40	10.80
Uric Acid :	39.16	33.61	18.89	8.34
Butter		66.34	14.02	19.64
Hogs Lard		69.00	9.66	23.34
Mutton Suet		62.00	14.00	24.00
Unctuous Matter of Biliary Calculi . . .		72.01	6.66	21.33
Spermaceti		81.00	6.00	13.00
Fish Oil		79.65	6.00	14.35

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* Annales de Chimie et Physique, tom. v. p. 290. Annals of Philosophy, vol. xi. p. 356. Gay Lussac observes, that in assigning these proportions of the elements from the products of the analysis, Berard proceeds on the assumption, that water is composed of 87 of oxygen, and 13 of hydrogen, while, according to the result, that two volumes of hydrogen are combined with one volume of oxygen, 88.3, and 11.7, are the proportions. This leads to an important correction, in reducing the proportion of hydrogen, and increasing that of oxygen.

CHAP. II.

OF THE ANIMAL PRODUCTS.

THE animal, like the vegetable products, may be reduced to a number of proximate principles characterized by certain distinctive properties. Yet this classification is much less perfect than it is with regard to vegetable matter: we are far from being able to place under it the various animal solids and fluids; and it is necessary, in the present state of animal chemistry, rather to give the history of these solids and fluids in the state of composition in which they exist, introducing under them the description of such proximate principles as have been sufficiently defined. Under this arrangement, the history of the Blood is first to be given, as the common source whence the varieties of animal matter are derived, and as containing some of the most important principles of which these are composed. The principal recent researches on this fluid, and on the principles connected with it, are those by Dr Bostock *, Marcet †, Brande ‡, and Berzelius ||.

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* Medico-Chirurgical Transactions, vol. i. ii. iv.

† Ibid. vol. ii.

‡ Philosophical Transactions, 1812.

|| Animal Chemistry, and Essay on Animal Fluids, Medico-Chirurgical Transactions, vol. iii. or Annals of Philosophy, vol. ii.

SECT. I.—OF THE BLOOD.

BLOOD, that fluid which circulates through the vessels of the animal system, sustains life, and affords the principles whence other products are formed, differs in its qualities, in the different orders of animals. In insects it is white or pellucid; in the more perfect animals, it is of a red colour. Its consistence is somewhat thick, and it has a saponaceous feel: it has a sweetish slightly saline taste, and a perceptible odour. Its specific gravity is from 1.03 to 1.05.

Though blood, as it circulates in the body, appears homogeneous, under the microscope it presents the appearance of particles of a globular form, diffused through a liquid. On being drawn from the blood-vessels, the apparent uniformity of its composition is also soon subverted: it separates into a fluid of a yellowish colour and slight tenacity, and into a coagulum more or less firm, of a dark red colour. This process is the Coagulation of the blood: the fluid part is the Serum, the solid the Clot or Crassamentum. By a farther examination, the latter is found to be a mixture or slight combination of two principles,—of a red matter, soluble in water, and therefore abstracted by washing the crassamentum; and of a white, solid, elastic, and fibrous matter, which remains. The former has been named the Colouring Matter, or the Red Globules of the Blood; the latter the Gluten or Fibrin. The proportions of these to each other vary in different animals, and in the same animal in different states of the system.

The cause of that spontaneous change of the blood which constitutes its coagulation, is not well ascertained.

Though it takes place more readily when the blood is at rest, and when the temperature is allowed to fall below the natural heat; yet it also takes place under the opposite circumstances, of agitation, and when its temperature is not reduced. Neither is the access of atmospheric air necessary, as the coagulation takes place *in vacuo*, as Mr Hunter ascertained. Experiments were stated by Luzuriaga [*], which seem to prove, that the coagulation takes place more rapidly when the blood is exposed to nitrogen, carbonic acid, or nitrous gas, than when exposed to oxygen or to hydrogen gas. These facts seem anomalous: and it has been affirmed by Davy, that when blood is exposed to these and other gases, there is no marked difference in the times of coagulation [†]. Some have ascribed the coagulation to the evolution of some gas, which, while it remained in the vessels of the animal, was retained by pressure, and which, escaping from the fibrin, disposed it to coagulate. But this is confirmed by no fact [‡]. It is singular, that the facility of coagulation in blood, flowing from a living animal, is influenced by the state of the vital powers. If it is received successively in different vessels, the last portion coagulates more quickly than the first; and Hewson remarked, that if faintness comes on, the blood drawn in that state flows with extreme difficulty, and coagulates almost immediately.

The spontaneous decomposition of the blood in its coagulation, affords the easiest method of discovering its immediate principles; and from our knowledge of these, we are better enabled to determine the nature of the changes which re-agents produce on the entire blood itself.

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[*] Dissertatio Inauguralis, Edin. 1786.

[†] Researches on Nitrous Oxide.

[‡] According to Vogel, a small portion of carbonic acid gas escapes from blood, when it is placed under the receiver of the air-pump, and the air is exhausted, (Annals of Philosophy, vol. vii. p. 56.). But there is no proof of its exerting any agency with regard to the coagulation.

The liquid formed by the coagulation, the Serum, as it is named, is slightly viscid and consistent, of a pale yellowish colour, and an insipid somewhat saline taste. Its specific gravity is about 1.028; or, according to Dr Bostock, 1.023. The quantity of solid matter dissolved in it, he estimates at about 12 per cent. It mixes with water in all proportions, losing, with a large proportion of water, its colour and taste. It is slightly alkaline, as it renders the syrup of violets green: this alkali, Rouelle discovered to be soda.

When the serum is exposed to a moderate heat, it forms a kind of consistent mass, more or less firm, but still tremulous, with a portion of interposed fluid. This takes place at a temperature of 160°, and it does not require the presence of the air. It is produced, by adding to the serum two or three parts of boiling water; but if the serum has been previously diluted with cold water, it does not happen. It is also occasioned by the addition of a number of substances, as by several acids, by salts having an excess of acid, by alkohol, and by several metallic oxides. This coagulation, especially as it is produced by heat, is a true analysis of the serum. As the substance which coagulates has all the properties of the white of an egg, it has been termed Albumen. It exists in many other animal products, and is indeed one of the most abundant proximate principles of animal matter, especially of the animal fluids and of the softer solids; it is therefore necessary that its properties should be fully stated.

Albumen (of which the white of the egg furnishes the best example) is distinguished by the following properties.

It is soluble in water, and is separated from it by coagulation, by heat, by alkohol, by acids, and several metallic oxides. After its coagulation, it is no longer soluble in water, unless by long boiling. It has been observed, that the coagulum separated by alkohol is more soluble than that separated by acids. It was supposed by Fourcroy, that the separation of this principle is owing to its receiving oxygen; but the fact, that it is precipitated by alkohol, while it is not by several substances containing oxygen and yielding it readily, as oxymuriate of potash, sufficiently refutes this opinion: Thenard has stated, that it takes place *in vacuo* as readily as in atmospheric air; he supposes the coagulation to be merely the result of the condensation of the albumen, and the insolubility of concrete albumen is owing to its being in this condensed state *. If albumen is dissolved in 8 or 12 parts of cold water, it is not coagulated by heat; but even when diluted with a large quantity, as with 1000 times its weight, the liquor when heated, though not properly coagulated, becomes opaque †.

Albumen is dissolved by the alkalis. Its solution by ammonia proceeds slowly, and is completed only in the course of several months. The solution is in the form of a viscid pulp, porous, and of a much greater volume than the original albumen. Potash and soda dissolve it with facility even in the cold: a quantity of ammonia is disengaged during the solution; a grey powder is precipitated, and the liquor is of a dark brown colour: they also dissolve it, even in its coagulated state.

Sulphuric, nitric, and muriatic acids coagulate albumen, and in a more concentrated state dissolve it. In the concentrated sulphuric acid, the solution goes on slowly. In the nitric acid the action is more rapid; it can scarcely, however, be termed a solution: a large quantity of elastic fluid is discharged, and an oily-like matter is precipitated, soluble in alkohol. Phosphoric and acetic acids, according to Berzelius, do not coagulate it.

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* Annales de Chimie, tom. lxvii. p. 320.

† Bostock, Nicholson's Journal, vol. xi. p. 247.

Albumen, when decomposed by heat, affords the usual products of animal matter. It also contains sulphur. The effect of the white of an egg in blackening silver has been long known; and Parmentier and Deyeux found, that on triturating albumen with a solution of silver, and digesting it in water with a gentle heat, sulphuret of silver is formed. Its residuum affords phosphate of lime.

In the analysis of animal matter, it is of importance to have tests, by which minute quantities of albumen may be detected, as it enters largely, as an immediate principle, into the composition of many animal products. Corrosive muriate of mercury is one of the most delicate, and at the same time the most accurate. If a very small portion of the albumen of an egg be added to a large quantity of water, on adding a few drops of the solution of the corrosive muriate, a milkiness, and at length a precipitate, is occasioned. Dr Bostock found, that by this test, albumen diluted with 2000 times its weight of water is detected. The acetate of lead, (Goulard's extract), and the nitrate of silver, likewise precipitate it; but they are less useful tests, as they act on other varieties of animal matter, which the muriate of mercury does not *. A solution of tannin produces, slowly, a yellow precipitate.

When albumen has been coagulated, its properties are considerably changed. It is no longer soluble in water: by drying it becomes brittle, hard, and semi-transparent. Digested in water, it becomes soft, but does not soon suffer any farther change. It is changed by the action of the acids. Nitric acid appears, from Mr Hatchet's experiments †, to convert it into a matter analogous to gelatin. The alkalis dissolve it, at the same time decomposing it and causing a formation of ammonia.

Albumen exists not only in the blood, but forms a con-

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* Nicholson's Journal, vol. xi. p. 247.

† Philosophical Transactions, 1800, p. 376.

stituent part of many of the soft fluids. From Mr Hatchet's experiments, it appears to be the basis of cartilage, shell, horn, and hair, and it enters into the composition of membrane, muscular fibre, and bone.

After the albumen has been separated by heat from the serum of the blood, there remains a portion of animal matter, with regard to the nature of which different opinions have been maintained. The liquor affording a precipitate with infusion of tannin, and becoming viscid by inspissation, the dissolved matter was supposed to be the peculiar animal principle named Gelatin, which exists as a constituent part of some of the soft solids, and is characterized by affording with water, in a certain state of concentration, a solution of a gelatinous consistence, and forming an insoluble compound with tannin. Dr Bostock found, however, that this fluid, the Serosity as it has been named, does not give any proper gelatinous appearance; and as albumen as well as gelatin forms a precipitate with tannin, this result it is evident is not conclusive. The peculiar test of albumen is that of being coagulated by corrosive muriate of mercury, which gelatin is not. The serum, after the separation of albumen from it by coagulation, Dr Bostock found, became quite milky, and formed a precipitate with this test, proving that a portion of albumen still remained dissolved in it; and when the whole of this was removed by the action of the muriate of mercury, it no longer yielded a precipitate with tannin. The conclusion followed, therefore, that gelatin does not exist in the serum, and that the appearances from which this had been inferred, arise merely from a small portion of uncoagulated albumen remaining in it. A minute portion of animal matter remains after the separation of the albumen by muriate of mercury, which Dr Bostock has considered as a peculiar principle, named Mucus, and distinguished by the properties of not being affected by corrosive muriate of mercury, or by tannin, but being precipitated by acetate of lead. It is probable, however, as has been shewn by Dr Pearson, that this is a residual portion of the albumen, the properties of which are not apparent from the dilution, or are modified by the action of the saline matter *.

The saline substances contained in the serum, and which remain after the separation of the animal matter, are not easily determined with perfect precision. Muriate of soda appears to be the one which is in largest proportion, and is discovered by its cubical crystals on evaporation: it appears also that a portion of muriate of potash is present, and the presence of this alkali in this, or in some other state of combination, is unequivocally proved by the tests of tartaric acid and muriate of platina, applied to the saline residue of the serum after incineration. The free alkali existing in the serum, was inferred by Rouelle to be soda, chiefly from his finding muriate of soda to be obtained from adding muriatic acid. Dr Pearson, from some experimental researches on serum, and several other animal fluids, concluded that the free alkali they contained is potash †. Dr Marcet, from other results, maintained the opinion, that soda is the uncombined alkali existing in these fluids, and that potash is present only in the state of muriate ‡. Berzelius agrees in the conclusion that soda is present in the serum in the state of sub-carbonate; he also finds muriates of potash and soda, lactate of soda, and phosphate of soda. Some other saline substances are obtained by incineration of the evaporated matter of the serum, particularly sulphate of potash in minute quantity, and earthy phosphates; but these Berzelius regards as products of decomposition, as they are yielded by the incineration of albumen alone. It is not improbable, however, that the earthy bases must exist in some state of saline

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* Nicholson's Journal, vol. xxxii. p. 47.

† Philosophical Transactions, 1809, 1810.

‡ Nicholson's Journal, vol. xxxi. xxxii. xxxiii.

combination. The quantities of these ingredients are so minute, and they are in such a state of intermixture, that it is difficult to establish the precise results with accuracy.

The following is the composition of the serum of the blood, as given by Berzelius: water 905, albumen 80, muriate of potash and soda 6, lactate of soda united with animal matter 4, soda, phosphate of soda, and a little animal matter 4.1. With this the analysis by Dr Marcet very nearly corresponds, his muco-extractive matter being the impure lactate of Berzelius. He finds in 1000 parts, water 900, albumen 86.8, muriate of potash and soda 6.6, muco-extractive matter 4, sub-carbonate of soda 1.65, sulphate of potash 0.35, earthy phosphates 0.60. According to Berzelius, the serum of human blood, to which his analysis applies, contains three times the quantity of muriates that the serum of ox blood does, owing, as he supposes, to the quantity of salt consumed by man. It also contains more muriate of potash.

From the composition and properties of the principles of the serum, we perceive the nature of the changes it produces, or which it suffers from certain chemical agents. Thus, from the alkali it contains, it changes the vegetable colours to a green; it is coagulated by heat, by alkohol, and acids, from the coagulability of the albumen; it is rendered thinner by the alkalis, from the solvent power they exert on the albuminous matter; gives a precipitate with tannin, from the combination of that principle with albumen; it reduces several of the metallic oxides when digested with them, and passes itself to the solid state,—a change probably owing to its albumen attracting oxygen. And when decomposed by heat, it affords carbonate and prussiate of ammonia, empyreumatic oil, carburetted and sulphuretted hydrogen gases, with carbonic acid gas; its residuum being charcoal, containing the salts which have been mentioned as being dissolved in this fluid.

The properties of the Crassamentum, or solid coagulum of the blood, are next to be considered.

It is of a dark red colour: by exposure to atmospheric air, or to oxygen, it acquires a more florid red hue, and it becomes darker on being exposed to hydrogen, carbonic acid, or any other gas, carburetted hydrogen excepted; this last gas, like oxygen, gives a more vivid colour. In all these cases the gas by which the change is effected seems to be absorbed, though not in considerable quantity. These changes take place, even when the coagulum is covered with serum. The change of colour is confined nearly to the surface; the crassamentum, when rendered florid by exposure to oxygen, appearing of a dark colour internally, when cut into.

The crassamentum exposed to the air does not immediately putrefy: it retains its colour and consistency for several days, if the temperature of the air is not high. If it be exposed to a moderate warmth, it is dried: it retains its dark red colour, and if kept in a dry place, may be preserved for a long time without decomposition. Decomposed by heat, it affords the same products as other animal substances; and the residual charcoal contains iron, with salts having lime and the alkalis for their bases, and containing phosphoric acid.

The crassamentum is not a homogeneous substance. If it be washed with water, by inclosing it in a linen bag, immersing it repeatedly, and pressing it gently, the water acquires a deep red colour, and there remains a fibrous matter, nearly white. By this simple analysis it is resolved into two distinct principles,—colouring matter, carried off by the water, and a solid fibrous substance, which remains. The former is named the Colouring Matter of the Blood; the latter the Gluten, Coagulable Lymph, or Fibrin.

The colouring matter, from microscopical observations, has been supposed to consist of round globules, which some have even imagined to be organized: it appears rather to adhere to these globules, and to be capable of being abstracted from them by water. It is the matter on which the gases act with peculiar energy. If it is exposed to atmospheric air, or oxygen, or even to substances capable of affording oxygen, if, for example, oxide of mercury is diffused through its watery solution, it acquires a florid hue: if exposed to hydrogen or carbonic acid, it is said to become of a brown or dark red colour. I have not observed any change of colour by passing through it carbonic acid gas.

Different methods are employed to obtain this colouring matter pure. By the process of washing it from the fibrin of the crassamentum, it is obtained in solution in water, and is slowly deposited. It cannot easily be obtained by evaporation, as, from the requisite temperature, it undergoes some change, losing its colour, and separating in brown flocculi: by slow evaporation however at a gentle heat, it is, according to Berzelius, procured without alteration. A method employed by Mr Brande, is to stir blood during its coagulation; the fibrin separates, and the colouring matter is diffused in the serum, from which it gradually subsides, being difficultly soluble in that fluid. Another process which has been more recently given by Vauquelin *, is to digest the coagulum of blood, from which the serum has been allowed to drain off on a sieve, in four parts of sulphuric acid diluted with eight parts of water, for five or six hours, at a heat of 160°: the liquid is to be filtered while hot, the residuum being washed with an equal quantity of hot water, this liquor is to be added to the other, and the whole is to be evaporated to one half; ammonia is then to be added, until a slight excess of acid only remains. The colouring matter, which had combined with the acid, is precipitated by the ammonia, and water is to be poured on it, and decanted off, until it cease

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* Annales de Chimie et Physique, tom. i. p. 10.

to give any precipitate with nitrate of barytes. The matter is then to be dried at a low heat. It is without taste or smell. Its colour is a deep black, with a resinous lustre and fracture. It assumes a deep red colour when mixed with water, but does not dissolve: it dissolves in acids and alkalis, and forms solutions of a purple colour; when heated it neither alters its form nor colour, and by an increase of heat is decomposed. There may be some room to doubt, whether, as obtained by this process, it does not suffer some alteration from the state in which it exists in the blood. According to Berzelius, the process is unnecessary, and does not succeed, and the best method is that merely of separation by water, and slow evaporation.

When submitted to examination in that state in which it may be supposed to have suffered least alteration,—abstracted from the crassamentum by washing with water, or by diffusion in the serum and subsidence from it, it is found to be apparently soluble in water, as it forms a liquor of a deep red colour, transparent, and which passes the filtre; yet the colouring matter slowly subsides from it. If the heat be raised to 170 or 190, it immediately separates in brown flocculi, and the liquor by filtration is obtained colourless. The addition of alkohol or of ether also renders the solution turbid, and a similar deposite is formed. Of this a portion is dissolved by digestion in dilute sulphuric and muriatic acids, and a part remains undissolved. The acids produce considerable changes on the colouring matter, in general combining with it, and forming compounds, insoluble or soluble according to the proportions. Sulphuric acid, diluted with eight or ten parts of water, dissolves it with the aid of heat, forming a purple solution, which remains permanent a considerable time; if more concentrated, it impairs the bright colour, and forms also an insoluble compound of a very dark colour, with an excess of acid. Muriatic acid poured on the colouring matter, renders one portion of it nearly insoluble, and of a brown colour; it dissolves another portion, forming a liquor of a dark crimson colour equally permanent, and which by evaporation affords a red coloured matter. Nitric acid, even much diluted, impairs the colour, and this with so much energy, that a few drops added to the sulphuric or muriatic solutions render them brown. Acetic and several of the other vegetable acids form solutions of a deep red colour, which, like the greater number of these solutions, exhibits a shade of green by transmitted light. The alkalis, either pure or in the state of carbonate, form solutions which are of a deep red, and extremely permanent; and these liquors may be evaporated nearly to dryness without losing their colour. The colouring matter forms combinations with some metallic oxides, as those of tin and quicksilver, so as to be abstracted by them from solutions in which it exists; it even abstracts these oxides from their salts, forming coloured precipitates; and by their medium as mordants, there is reason to believe that it may form a permanent dye: with others, as oxide of lead, it does not unite; nor does it form a permanent combination with alumina. These facts have been principally ascertained by Mr Brande *.

The colouring matter of the blood seems to be possessed of specific properties, its relations and habitudes being peculiar. Berzelius has supposed it to be the same as fibrin, except in colour, and in not coagulating; an opinion rather vague, since these are in fact properties sufficient to constitute an essential distinction, and there are others equally important.

The colour has been supposed to depend on the presence of iron, a metal which in so many cases gives tints of colour, where it is present even in minute quantities. The existence of this metal in the blood had been known to chemists. Lemery and Menghini discovered, that from

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* Philosophical Transactions, 1812.

blood dried by a very gentle heat, it could be extracted in a magnetic state. Bucquet found, that the colouring matter separated from the crassamentum, dried and decomposed by heat, gave a residuum containing iron. Parmentier and Deyeux supposed that the alkali of the blood retained oxide of iron in solution. Sage and Gren supposed, that the iron existed in the blood in combination with phosphoric acid; and Fourcroy and Vauquelin gave experiments, by which they suppose this to be established. It exists, according to these chemists, in the state of sub-phosphate of iron, a compound which they describe as being of a brownish red colour, not very soluble in acids, but soluble in alkalis; and it is by the action of the free alkali of the blood that they supposed it to be dissolved. They accordingly stated, that this sub-phosphate of iron is dissolved in the serum of the blood, or in the white of an egg, even without heat, and that it forms a red colour similar to that of the blood. A little pure alkali accelerates this solution, and renders its colour more perfect and lively *.

The opinion that the colour of the blood depends on iron, had not been altogether received. It had been called in question by Dr Wells, though not on very valid grounds; and the opinion suggested, chiefly from optical considerations, that "blood derives its colour from the peculiar organization of the animal matter of one of its parts †." The experiments of Fourcroy and Vauquelin have not been established by others, but have afforded different results. Berzelius found, that sub-phosphate of iron, mixed with serum, gives it merely a brown colour, and instead of being dissolved, soon subsides, or may be separated by a filtre; neutral phosphate of iron mixed with serum, does not dissolve, and the addition of an alkali produces the sub-phosphate, which remains equally inso-

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* System of Chemical Knowledge, vol. ix. p. 208.

† Philosophical Transactions, 1797, p. 427.

luble. If even phosphoric acid be added to dissolve the sub-phosphate in mixture with the serum, a rust-coloured liquor only is formed; if a small portion of alkali be added, it precipitates a little albumen, which is re-dissolved by a slight excess of alkali; and then the liquor loses its red colour, and the sub-phosphate falls down. In a word, says Berzelius, I have found no method of combining albumen with sub-phosphate of iron or with any other salt of this metal, so as to produce a compound similar to the colouring matter of the blood. The albumen he found dissolves oxide of iron even in larger quantity than what exists in the colouring matter; but this solution is yellowish; and the oxide of iron is discovered by the usual reagents; it is easily obtained in combination with the acids which precipitate albumen; and if prussiate of potash be added, though it does not affect the colour, alone, yet on the addition of a little muriatic acid, a rich blue is formed. No such effects are obtained from the solution of the colouring matter of the blood,—neither infusion of galls nor prussiate of potash affect it in the manner in which they act on iron, and not even, as Vauquelin has shewn, when it is dissolved in diluted acids, and these tests added to the solutions. Neither can any iron be extracted from the colouring matter by the action of acids, as Berzelius found, but only by incineration, a proof that it exists in no state of loose combination, but only as an ultimate element. And in this state it does not appear how it should exclusively give the colour, and still less render this colour liable to be affected by the gases and by other re-agents *. The quantity too is extremely minute. Dr Pearson collected 100 grains of dried colouring matter from about 20 ounces of blood; by incineration it afforded 2½ grains of matter, from which not above half a grain of oxide of iron could be obtained. Is it probable, he adds,

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* Treatise on Animal Chemistry.

that from this 20 ounces of blood should derive their colour? Mr Brande likewise found the quantity to be extremely minute, and to be not larger than what was obtained from the colourless coagulum; whence he was led to the conclusion, that the colour does not depend on iron, but on the composition of the animal matter. Vauquelin, in the memoir already referred to, confirmed Mr Brande's experiments, and adopted the same conclusion.

The earlier experiments, however, on this subject, seemed to leave no doubt, that iron can be obtained in very sensible quantity from the colouring matter of blood by incineration. And Berzelius had found the proportion to be larger than it appeared to be from the more recent investigations,—about five grains of ashes being procured from 400 of colouring matter, of which half the weight was oxide of iron. He has since, in consequence of Vauquelin's experiments, resumed the investigation *. The process employed by this chemist to procure the colouring matter he found imperfect, a considerable portion not being dissolved by the acid, or rather, though combined with a portion of acid, not being soluble in the liquid, so as to pass the filtre; and this insoluble portion was of a very deep colour, and afforded by calcination, a residue composed entirely of red oxide of iron. The quantity of iron obtained from the colouring matter he found, on a repetition of his experiments, to be the same as that which he had formerly found. It can be obtained, however, in no other way than by incineration; hence it is evident it does not exist as oxide of iron in any usual state of combination in the blood; and it is more probable, as he suggests, that iron exists as one of the ultimate elements of colouring matter, in direct combination with the others. How far the colour depends on it, it is not easy to determine. But the circumstances, that it is not found to

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* Annales de Physique et Chimie, tom. v. p. 42.

the same extent, or even not sensibly in the white solids, such as albumen and fibrin, and that minute quantities of iron often give rise to colour in other combinations, render the affirmative not improbable.

The colouring matter decomposed by heat, affords, according to Vauquelin, carbonate of ammonia, and a purple oil, but scarcely any elastic fluid. The residue is a charred mass, soluble neither in acids nor alkalis. According to Berzelius, the charcoal of 400 grains of colouring matter, afford by perfect incineration 5 grains of ashes composed in 100 parts, of oxide of iron 50, sub-phosphate of iron 7.5, phosphate of lime with a small quantity of magnesia 6; pure lime 20, carbonic acid and loss 16.5. According to the same chemist, 100 parts of the crassamentum contain 64 of colouring matter.

The other principal constituent part of the crassamentum, the Fibrin, remains after the colouring matter is carried off by washing: it can also be obtained from the general mass of blood, by agitating it with a rod in an open vessel: the other principles are mixed together, and the fibrin adheres to the rod; it forms those concretions named Polypi, sometimes found in the vessels of animals after death; and in certain diseases, it is disposed to separate from the other principles, giving rise to the appearance named the Inflammatory Crust, or Buffy Coat. It is it which gives to the blood the property of coagulating spontaneously. Its quantity, according to Fourcroy and Vauquelin, amounts at a medium to 0.0028. It is contained in many other animal products, as in the muscular fibre, of which it forms the basis, and is one of the best defined proximate principles of animal matter.

Fibrin is a solid white substance, free of taste or smell, of a fibrous texture, tough, and somewhat elastic: it hardens and contracts, on exposure to a moderate heat. It is insoluble in water, except at such a high temperature as that obtained by pressure in Papin's digester; or after long continued boiling, when a small portion of matter is found to be dissolved. Moistened with water, it softens, swells, and begins to putrefy: it suffers a similar change in a damp atmosphere. This, however, applies only to the fibrin of blood, which has probably some other matter attached to it: for Hatchet found, that fibrin obtained by repeatedly washing, and boiling the muscular fibre with water, is not very liable to putrefaction.

Fibrin is dissolved by the alkalis, but is at the same time decomposed. Potash or soda acts upon it at common temperatures, renders it transparent and gelatinous, and at length soluble: vapours of ammonia are disengaged, and a greyish matter is precipitated, which is carbonaceous. Ammonia requires a temperature equal to 170°, to enable it to dissolve it.

The acids exert a considerable action upon fibrin. Acetic, and several of the vegetable acids, dissolve it, first rendering it transparent and gelatinous: the solution is decomposed by the alkalis, and even by water; but the precipitate has not the properties of the original matter, being, in particular, soluble in water. It is given as a test of fibrin by Berzelius, that when dissolved by boiling in dilute acetic acid, the solution yields a yellow precipitate on the addition of prussiate of potash. Muriatic acid has been said to dissolve it. According to Berzelius, the strong acid aided by heat decomposes it, producing a red or violet coloured solution; the diluted acid scarcely dissolves any portion of it, but by boiling converts it at length into a gelatinous mass, which, after repeated affusions with water, becomes soluble in tepid water. Sulphuric acid decomposes it, throws down a carbonaceous powder, and forms acetic acid: the same acid diluted, and digested with fibrin, acquires a red colour; and according to Berzelius, all these acids form two compounds with fibrin, one with an excess of acid which is insoluble, and one which, when this excess is removed by affusion with water, becomes neutral, and at the same time soluble. Nitric acid, diluted with a large quantity of water, disengages nitrogen gas, which proceeds entirely from the fibrin, as it was ascertained by Berthollet, who first observed the phenomenon, that the acid is not decomposed. The residuum is principally oxalic acid, with a small portion of malic and acetic acids, and a portion of fatty matter. When the nitric acid is undiluted, it suffers decomposition, and nitrous gas, mixed with nitrogen, is disengaged. The action of nitric acid, however, on fibrin, is much diversified, according to its energy. If the action be slow, the fibrin, as Hatchet found, passes into a state analogous to gelatin *. If heat is applied, the fluid becomes yellow, a fatty substance is formed, and it appears, from the experiments of Fourcroy and Vauquelin on muscular fibre, to be afterwards stated, that a principle, analogous to amer, yellow, bitter, and acrid, is produced. By the continued affusion of water, this becomes orange. Berzelius considers these two products as compounds of nitric acid and fibrin,—the one of a pale yellow colour, having an excess of acid, the other of an orange hue, being neutral.

Fibrin exposed to heat, is decomposed. An empyreumatic oil, of offensive smell, distils over, which is followed by carbonate of ammonia, and very fœtid gases, probably compounds of hydrogen with nitrogen and phosphorus: a charcoal remains, dense and brilliant, difficult of incineration, and containing phosphate and carbonate of lime. It seems, of any proximate principle of animal matter, to contain the largest proportion of nitrogen, as it affords the largest quantity when acted on by nitric acid. It appears also to contain the largest quantity of carbon, as the charcoal left in its decomposition by heat is more abundant, according to Hatchet's observation, than that from albumen or gelatin. The results of its analysis by Gay Lussac and Thenard, inserted in the table at the end

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* Philosophical Transactions, 1800, p. 591.

of the preceding chapter, accordingly give a larger quantity of nitrogen and carbon in its composition, and less oxygen, than in that of either of these principles.

After pointing out the proximate principles of which the blood is composed, it remains to state the chemical properties of the entire fluid.

Blood newly drawn is soluble in water, as it can be diffused through it without any alteration, and this dilution prevents its spontaneous coagulation. If the mixture, however, be heated, flakes separate, consisting of the albumen, and the colour is changed to a brown. The liquor, separated from the coagulum, yields, according to Fourcroy, a yellow bitter matter, by evaporation.

Acids added to blood decompose it: they render its colour brown, and produce coagulation: and form insoluble compounds with its principles. The nitric acid disengages nitrogen gas; the oxymuriatic acid renders it black. The alkalis, instead of coagulating the blood, render it more thin, and prevent its spontaneous coagulation, evidently from their solvent power on the albumen and fibrin. The neutral salts frequently alter the colour of blood, and a number of them retard its coagulation. The metallic salts, in general, decompose and coagulate it: alkohol, and even some vegetable principles, as starch and gum, likewise produce coagulation: tannin thickens and renders it black.

When the watery part of the blood is withdrawn by gentle evaporation, a mass is obtained of a dark brown colour, which, if kept humid, passes into putrefaction, and evolves very offensive products. If dried more thoroughly, it is obtained in the state of a black powder, which in a dry atmosphere may be preserved with little alteration. When exposed to heat it softens, swells, and in the open air inflames feebly, exhaling a fœtid smoke. The products in this decomposition are, according to Fourcroy, an ammoniacal liquid, carbonate of ammonia, and a dense fœtid vapour, oily and inflammable: after these the vapour of prussic acid is recognizable by its smell, and lastly phosphoric acid. The residuum consists of oxide of iron nearly reduced, phosphate of lime, and muriate of soda. When the decomposition of blood by heat is performed in close vessels, there first distils over a quantity of water of a faint odour; when urged by a stronger heat, this is followed by a liquid holding dissolved carbonate of ammonia mixed with oil: this oil comes over more copiously as the decomposition proceeds, is thick, of a dark colour, and fœtid; it is accompanied by carburetted and sulphuretted hydrogen gases. The coal which remains in the retort is spongy, of a brilliant semi-metallic appearance, and difficult of incineration; it contains, along with charcoal, iron nearly reduced, phosphate, muriate, and carbonate of soda, and phosphates of iron and lime.

The preceding history of blood has no reference to the different states in which it exists in the animal system. Such differences, however, exist; the blood in the arteries of an animal is not the same as that in the veins; and the nature of this difference is to be explained. This includes the chemical history of the function of respiration, by which the conversion of venous to arterial blood is effected.

The blood which returns to the heart by the veins, from the extremities of the arteries, is of a dark red colour verging to purple. When received into the right ventricle, it is thrown into the pulmonary artery, and conveyed to the lungs, where it circulates through extremely minute vessels, over a surface which it has been calculated is at least equal to the whole external surface of the body. During this circulation, in which it is exposed to the atmospheric air, alternately taken in and thrown out by respiration, it changes its colour, becoming of a more vivid vermilion hue. It is returned by the pulmonary veins to the left side of the heart; is thrown into the aorta, and distributed through the arteries over the body. In the arteries it preserves its florid red; but, in their minute extremities, it suffers a change opposite to that which it had sustained in the lungs: it acquires the purple colour, and constitutes venous blood, which is returned to the right side of the heart.

When we examine chemically the properties of arterial and venous blood, we discover no other difference between them than that of colour. The difference of colour, however, points out some difference in composition, though it may be too slight to be detected by analysis; and when we examine the phenomena of respiration, which are intimately connected with the change of venous to arterial blood, we find that such a difference must exist.

In respiration atmospheric air is received into the lungs, and retained for a short time. When expired, its composition is found to be altered. It has lost a considerable part of its oxygen, and it contains a quantity of carbonic acid. The changes which it has suffered are connected with the conversion of the venous into arterial blood, and consequently must be accompanied with correspondent changes in the composition of that fluid.

Dr Black seems first to have observed, that the air expired from the lungs contains carbonic acid, from finding a milkiness to be produced when it is transmitted through lime-water. Priestley some years afterwards considered respiration as analogous to what he named phlogistic processes in general, that is, to processes in which oxygen is consumed; the air being rendered incapable of supporting combustion or respiration. Lavoisier soon after ascertained, that during respiration, the oxygen of the inspired air is in part consumed; and that carbonic acid is formed.

When these discoveries were made, it became an object of importance to determine the extent of these changes; in other words, the quantity of oxygen consumed, and that of carbonic acid produced. With regard to this, however, the results of the experiments of different chemists have been extremely discordant; partly from the changes being influenced by the volume of the lungs, the state of the circulation, the nature of the food, the state of the assimilatory organs, and the temperature, all of which it is not easy to obtain uniform, and partly from the experiments having often been performed, not on natural respiration, but on air repeatedly inspired; or by confining an animal in a quantity of air, when there was not only this source of error, but another in the effects of cutaneous transpiration.

The earliest experiments were those by Crawford and Lavoisier. Crawford found, that when 20.1 grains of carbonic acid gas were formed, 18.9 grains of oxygen were consumed *; and Lavoisier obtained a result not far different, 26 grains of carbonic acid being produced, when 23.2 grains of oxygen were consumed †: in both cases, therefore, a larger proportion of oxygen disappearing than was necessary to form the quantity of carbonic acid expired. The experiments, however, were made in the exceptionable manner of confining an animal in the air respired, and cannot therefore be relied on as indicating the proportions of the changes in natural respiration.

Goodwin, by examining the air received into the lungs in one inspiration, found, that when 12 cubic inches were breathed, the air expired had lost 1.56 of oxygen, while it had acquired 1.32 of carbonic acid; so that when 22 parts of carbonic acid were produced, 26 parts of oxygen by measure were consumed ‡; but this mode of experiment is liable to fallacy, from the small quantity of air operated on, and from this quantity not being the whole of what is submitted to the action of the blood in the lungs in a single respiration.

Priestley, in some experiments subsequent to those which

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* Crawford on Animal Heat, p. 547.

† Annales de Chimie, tom. v. p. 264.

‡ Connection of Life with Respiration, p. 51.

he first made on respiration [*], found the proportion of oxygen consumed to that of carbonic acid formed higher than that above stated, attended at the same time with a great diminution of volume. But the same air was repeatedly inspired, and hence, from the difficulty attending it, the due proportion had not been thrown from the lungs, at the concluding expiration.

In a memoir on respiration, in the Memoirs of the Academy of Sciences for 1789, by Seguin and Lavoisier, it is stated, that, from experiments by the former chemist upon himself, the mean consumption of oxygen in respiration is in the course of twenty-four hours 24 cubic feet, or 2 lbs. 1 oz. 1 dr. and that, in the same time, the quantity of carbonic acid formed is equal to 2 lbs. 5 oz. 4 dr. [†] But in a second memoir, in the Transactions of the Academy for 1790, the consumption of oxygen is stated at a little more than 22 cubic feet in twenty-four hours, or 33 ounces 1 drachm and 10 grains, while the quantity of carbonic acid formed in the same time is stated at only 8 cubic feet 6 cubic inches, or 17 ounces 7 dr. 4 gr. Such a discordance prevents any confidence from being placed in either result.

From some experiments by Davy, performed on natural respiration, it follows, that when 31.6 cubic inches of oxygen are consumed, which is in the course of respiration for a minute, 26.6 cubic inches of carbonic acid are produced [‡].

Some years prior to these, I executed some experiments in a similar manner [||]. A thin varnished bladder was furnished with a stop-cock, and by a little practice, the facility of inspiring *from* the external atmosphere and *into* the bladder was acquired; the stop-cock being shut at the inspiration, and being opened, by turning it with one hand while the nostrils were closed with the other, at the succeeding expiration. The quantity of air expired, amounted in thirty seconds to 265 cubic inches: the quantity of carbonic acid gas contained in it was found to amount to 16 cubic inches. The oxygen in the residual air amounted to 44.1 cubic inches. To determine what quantity had been consumed, it remained to ascertain the quantity contained in the air inspired; but as this, from the manner of making the experiment, by breathing from the atmosphere, was not measured, the quantity of it was inferred, from the quantity expired, adding to this $\frac{1}{50}$ of volume to compensate for the diminution, which, according to the experiments of Lavoisier, Goodwyn, and others, the air sustains in respiration. This makes the quantity of air inspired equal to 270 cubic inches, containing 63.4 cubic inches of oxygen. The expired air contained 44.1 cubic inches, and consequently 19.3, or, making allowance for a correction to bring it to the standard atmospheric pressure and temperature, 19 cubic inches of oxygen had been consumed. It follows, therefore, that in the course of a minute 38 cubic inches of oxygen had been consumed, and 32 cubic inches of carbonic acid formed *.

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[*] Philosophical Transactions, vol. lxxx. p. 108.

[†] Mémoires de l'Acad. des Sciences, 1789, p. 577.

[‡] Researches on Nitrous Oxide, p. 434.

[||] Records of the Medical Society of Edinburgh for 1798.

More lately, a series of experiments was made on this subject by Messrs. Allen and Pepys †, with an apparatus in which the volume of the air could be measured with great accuracy, and in which a large quantity (3 or 4000 cubic inches) could be respired; so that the source of error to which experiments on a smaller scale are liable, from the influence of the residual air in the lungs, is much diminished. In the formation of carbonic acid by the com-

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* If there is no diminution of the volume of the air in respiration, then the quantity of oxygen consumed amounts only to 36 cubic inches in a minute.

† Philosophical Transactions, 1808.

bination of charcoal with oxygen gas, there is reason to believe, that there is no change of volume. To determine, therefore, the relative proportions of oxygen gas consumed, and of carbonic acid gas formed in respiration, and thus ascertain whether a portion of oxygen is consumed besides what is necessary to form the carbonic acid expired, nothing more was necessary than to discover whether the volume of the air inspired experienced any change. From their experiments, a slight diminution appeared to be produced in the air by respiration. It was much smaller, however, than that observed by former chemists; and they considered it as arising from the difficulty of bringing the lungs into the same state at the end of the experiment as at the commencement. They accordingly found, that when the experiment was continued for a long time, instead of the diminution continuing to bear the same relative proportion to the quantity of air which had passed through the lungs in that time, it had become less; so that in an experiment in which the respiration continued 24½ minutes, and in the course of which 9890 cubic inches of atmospheric air had been inspired, the expired air measured 9872, or there was a deficit on this large quantity of only 18 cubic inches. There is therefore apparently no consumption of oxygen beyond what is necessary to form the carbonic acid expired. The quantity of carbonic acid expired must be liable to variation in different individuals, and under different circumstances: it is greater, for example, when respiration is performed quickly; in this case they found the quantity to be 32 cubic inches in a minute; but in respiration as nearly natural as possible, they estimate it on an average at 26.6 cubic inches, at the temperature of 50°. And as oxygen gas occupies the same space when converted into carbonic acid gas as it does in its pure state, this is also the quantity, estimated by volume, of the oxygen consumed in the same time.

These experiments agree nearly with the most accurate of those formerly made, as to the quantity of carbonic acid formed in respiration, and differ chiefly in the result, that there is no diminution of the air, and therefore no oxygen can be supposed to be absorbed into the system. There can be no doubt but that the source of error which gave rise to the opposite conclusion, might exist in experiments performed on a small scale; and that it is best obviated in performing the experiment on a large scale; but as, after all, a small diminution was perceived in their experiments, and as also in respiration, under other circumstances, a quantity of oxygen appears to be absorbed into the system, as I shall have immediately to state, some doubt may remain, but that there is such an absorption, to a small extent, in natural respiration. Berthollet more recently found a diminution in the volume of the air, but not to a great extent; and as it was variable, and the experiments were made on an animal confined in a quantity of air, the result is doubtful. In exposing blood to atmospheric air, the abstraction of a portion of its oxygen was replaced by an equal volume of carbonic acid gas *.

It is a just observation by Berzelius †, that the quantity of carbonic acid gas stated to be produced in respiration is, according to the usual estimates, such as to involve a difficulty with regard to the quantity of carbon which must be inferred to be abstracted from the system, or rather the conclusion which must necessarily be drawn with regard to this, affords a proof that these estimates are incorrect. Taking that of Allen and Pepys, that 26.6 cubic inches of carbonic acid are expired by an adult in a minute; this implies a consumption of 11 ounces nearly of carbon in 24 hours, a quantity certainly exceeding greatly the quantity contained in the average proportion of food consumed in that time. The estimate, therefore, of the production of

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* Mémoires d'Arcueil, tom. ii. p. 455.

† View of Animal Chemistry, p. 59.

carbonic acid is undoubtedly stated too high in this and in all the other series of experiments, arising partly perhaps from their having been made under circumstances when the production is greatest, but principally probably from the difficulty of imitating natural respiration, and the tendency there is to relieve the uneasy sensation which attention to the act of respiration causes, by making the respirations either more frequent, or if slow more full; whence both the formation of carbonic acid may actually be rendered greater, and at least the proportion, when the estimate is extended to 24 hours, is augmented. The quantities of oxygen consumed, and carbonic acid formed, are also considerably influenced by circumstances, as is to be immediately stated.

The air expired from the lungs, always contains watery vapour, as is evident from its condensation when we breathe in a cold atmosphere. The quantity it is difficult to estimate with accuracy. Dr Menzies breathed into a large allantoid, which had been weighed in a delicate balance; the air was allowed to remain in it, to allow of the condensation of the vapour, and from the weight the allantoid gained, he concluded, that 2 grains of vapour are expired in a minute. Mr Abernethy, by breathing into a glass vessel adapted to condense the water, found the quantity equal to 3 grains in a minute *. By exposing acetate of potash, a salt very deliquescent, in a thin bladder into which air was breathed for half a minute, I found reason to conclude, comparing the result with the increase of weight which the salt gained from the same volume of atmospheric air, that 3 grains of watery vapour are expired in a minute.

It is lastly to be determined, what is the influence of the nitrogen of the atmosphere in respiration. With regard to this different conclusions have been formed. Lavoisier,

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* Physiological Essays, p. 141.

in his early experiments, considered it as suffering no change *. Priestley, in the experiments already referred to, in which he breathed the same air repeatedly, observed an apparent consumption of nitrogen; but he afterwards inclined to the supposition, that the deficiency arose from the greater proportion of it remaining in the lungs after the process than before. Davy concluded, that nitrogen is consumed in respiration, a quantity disappearing equal to about two-tenths of a cubic inch at each natural respiration, 13 cubic inches being the quantity of air taken into the lungs; and as the number of natural inspirations amounted in a minute to 26 or 27, it followed, that in that time 5.2 cubic inches of nitrogen are consumed,—a result which was confirmed by continued respiration, as well as by the respiration of animals confined in a portion of air, though in the latter case the quantity consumed appeared to be less †. This absorption of nitrogen appeared to be confirmed by other experiments. It was observed by Dr Henderson, in breathing a portion of air repeatedly from and into a gazometer ‡; and it seemed likewise to be established by the experiments of Pfaff ||.

These experiments, however, are not free from fallacy, particularly those where the same quantity of air was repeatedly breathed; for, as Mr Ellis has justly observed §, the respiration as it proceeds becomes more laborious, and is terminated by a feeble expiration, whence the due proportion of air is not thrown from the lungs. There appears, therefore, a diminution; and accordingly this is always greater the longer the air is respired. In experi-

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* Mémoires de l'Acad. des Sciences, 1777. Mémoires de la Société de Medicine, 1783.

† Chemical Researches, p. 434.

‡ Nicholson's Journal, vol. viii. p. 40.

|| Ibid. vol. xii. p. 249.

§ Inquiry on Vegetation, Respiration, &c. p. 114.

ments, too, in which this source of error is avoided, as those of Allen and Pepys, there is no apparent consumption of nitrogen. The same result is stated to have been obtained in the last experiments of Lavoisier and Seguin, "there being neither disengagement, nor absorption of nitrogen gas, during respiration [*]." From the experiments of Vauquelin, Spallanzani, and Ellis [†], it also appears, that there is no sensible consumption of nitrogen by the respiration of the lower orders of animals, while there is the usual consumption of oxygen and formation of carbonic acid.

Messrs. Allen and Pepys have even inferred, from some experiments [‡], that there is an evolution of nitrogen in respiration, nitrogen gas continuing to be found in the expired air when oxygen gas is respired for some time; and though much of this might arise from the operation of the residual air of the lungs, yet, on comparing the capacity of the lungs with the quantity of nitrogen evolved, they found more than could be derived from this source. In one experiment on a Guinea pig, confined in a quantity of atmospheric air, at the end of an hour and twelve minutes, the increase of nitrogen in the air was even more than equal to the cubic contents of the body of the animal. They concluded, therefore, that when oxygen gas is respired, a portion of nitrogen is given off from the blood.

There is, however, every probability that the nitrogen appearing in these experiments is derived from the residual air of the lungs; and Mr Ellis has assigned a cause whence the large quantity of it can be explained,—that of the condensation probably of the air in the bronchial cells. These are in immense number, and are of diameters extremely small. If they have any degree of contractile power, this may produce condensation of the air they contain. But independent of this, it is well known, as he remarks, that a strong attraction or *adhesion* is exerted between air and the surfaces of bodies; the more therefore the surface is increased, the greater must be the effect from this attractive force. Hence, under the extensive surface of the cells of the lungs, it must operate with great effect, and reduce considerably the volume of the air: and it may be aided by the attraction exerted by the humid surface to the aërial matter. All the phenomena, as he has shewn, accord with this view *.

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[*] Mémoires de l'Acad. des Sciences, 1789, p. 574.

[†] Inquiry, &c. p. 87. 88.

[‡] Philosophical Transactions, 1809.

It remains to take a view of the theories that have been proposed to account for the changes resulting from the action of the air in respiration, and by which the blood is at the same time converted to the arterial state.

Priestley considered these phenomena as owing to the disengagement of phlogiston from the blood in the lungs, and its combination with the air †, a theory modified and rendered more comprehensive by Crawford ‡. Regarding hydrogen as the phlogistic principle, and supposing it to exist in the blood in that state in which it is disengaged from vegetable substances by heat, combined with carbon, Crawford supposed that this hydro-carbon, as it was named, is communicated to the blood in the extreme vessels, by which the conversion from the arterial to the venous state is occasioned; that in the lungs it is given out, and in its nascent state combines with the oxygen of the air, and forms the carbonic acid gas and watery vapour expired, while the blood deprived of it returns to the arterial state. Lavoisier also supposed, that the carbonic acid gas and watery vapour of the expired air are formed by the combination of carbon and hydrogen from the blood with oxygen in the lungs.

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* Farther Inquiries into Vegetation and Respiration, p. 506.

† Philosophical Transactions, 1776.

‡ Experiments and Observations on Animal Heat.

He had likewise suggested, that the combination of oxygen with carbon might take place in the course of the circulation *; that the oxygen which disappears in respiration may be absorbed by the blood, while carbonic acid may be given out fully formed. This hypothesis was endeavoured to be established by Hassenfratz and Lagrange †. From the facts that venous blood exposed to oxygen acquires a vivid red colour, which soon changes to a purple hue, and that arterial blood placed *in vacuo*, or in contact with any gas which does not contain oxygen, quickly assumes the dark purple colour, they concluded, that the florid red colour of the blood is the result of the absorption of oxygen, while the dark venous colour arises from the intimate combination of this oxygen with a portion of the carbon and hydrogen which the blood contains. According to this opinion, oxygen is absorbed by the blood in the lungs; remains in the arterial blood for a time in a state of solution or loose combination; but passes gradually, in the extreme vessels, into more intimate combination with carbon, forming carbonic acid, in consequence of which the blood passes to the venous state; and from this venous blood the carbonic acid is disengaged in the lungs, and a new portion of oxygen absorbed.

These two hypotheses have divided the opinion of physiologists. They are both, however, defective. No proof is given, in the system of Crawford, of hydro-carbon being communicated to the blood in the extreme vessels; nor is it easy to imagine any source whence in an insulated state i can be derived; for, although it was imagined by Crawford, that it may have its origin in the solid parts of the system being absorbed, this is refuted by the considerations, that this absorption is performed, not by the veins, but by the lymphatics; that it is not limited to carbon and hydrogen; that to whatever extent it may be carried, the blood must, in a state of health, deposite as much as is removed; and that there is no cause by which the carbon and hydrogen can be separated from the other elements, and be brought into binary combination. And, in the theory of Hassenfratz, though it were granted, that a portion of oxygen is absorbed by arterial blood, there is no proof that this is combined merely with carbon, and that carbonic acid, the result of this combination, is contained in venous blood.

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* Memoires de l'Acad. des Sciences, 1777, p. 191.

† Annales de Chimie, tom. ix. p. 261.

Neither are the changes which these hypotheses suppose, analogous to the usual chemical operations of the animal system, or connected with the purposes which the blood serves in its circulation. When the general facility of combination in the principles of animal matter, and the tendency which the actions of the vessels have to form them into ternary or quaternary compounds, are considered, there is little probability in the assumptions of either hypothesis,—of the one, that oxygen should be absorbed by the blood in the lungs, without altering its composition; that it should be merely combined with carbon, in the proportions necessary to form carbonic acid; and that this carbonic acid, without affecting the ultimate composition of the blood, should be carried the whole length of the venous circulation, and thrown out at the lungs;—or of the other, that carbon and hydrogen should be brought into a state of binary combination in the extreme vessels, and should be held merely dissolved by the venous blood, until acted on by the oxygen of the air in respiration. And still less are these changes connected with the known changes which the blood suffers; for no relation is traced between the processes of assimilation or of secretion, and the supposed communication of hydro-carbon, or the combination of carbon and oxygen, in the extreme vessels.

In any theory of respiration, the conversion of arterial into venous blood ought to be considered as connected with these processes; and this conversion, as well as that of venous into arterial blood, must be regarded as arising from changes in the ultimate composition of the proximate principles of the blood, not from the alternate communication and abstraction of a principle which it holds dissolved in it, in what is termed a state of loose combination. Conformable to this view, I have given the following explanation of these phenomena.

The blood is the source whence the animal products are formed. This expenditure is supplied by the chyle, a fluid less completely animalized than the blood. The peculiar character of animal matter, with regard to composition, is a large proportion of nitrogen, and a diminished proportion of carbon. It may therefore be inferred, that in the extreme vessels, where the animal solids and fluids are formed, the general process will be the separation from the blood of those elements of which animal matter is composed; and that therefore carbon, which enters more sparingly into its composition, will exist in the remaining blood in an increased proportion. This is accordingly the general nature of *the conversion of arterial into venous blood.* Nitrogen, hydrogen, and other elements, are spent in the formation of new products, and the proximate principles of the blood remain with an increased proportion of carbon. In this state it is exposed to the atmospheric air in the lungs, the oxygen of which abstracts its excess of carbon. and forms the carbonic acid expired, and this constitutes *the conversion of venous into arterial blood.* There is no proof that any combination of the oxygen of the air with the hydrogen of the blood takes place. The supposition that it does, and that this is the source of the watery vapour expired, originated merely in the hypothesis of Crawford. And the degree of evaporation from a moist surface, so extensive as that of the internal surface of the lungs, at the temperature of 96°, is adequate to account for the whole of the watery vapour expired.

The conversion of arterial into venous blood, is thus considered in connection with the other chemical changes in the system, and is subservient to them. In the extreme vessels, the constituent principles of the blood are expended in the nourishment of the solid fibre, and in the formation of the secreted fluids. Of these principles, carbon is contained in the smallest proportion in these solids and fluids; it must therefore remain in excess: hence the necessity of the application of oxygen to the blood in the lungs to remove it, and the origin of the carbonic acid uniformly discharged. We thus, too, trace the process of animalization from the reception of the aliment to its completion. All animals live directly or indirectly on vegetable matter. The principal difference in the composition of vegetable from that of animal substances, is in the former containing a larger proportion of carbon. Respiration is the function by which this difference is established. The aliment received into the stomach, is formed into a fluid capable of assimilating with the blood. It is conveyed to the lungs, and loses part of its carbon, or is partially animalized. It is then distributed through the system, and, in the extreme vessels, along with carbon, parts with so much hydrogen, oxygen, nitrogen, and other elements, as to leave carbon predominant.

It might be supposed, that in any view such as this, there must be some difficulty in conceiving that oxygen gas should combine with carbon at a temperature lower than that in general necessary for their union, and this, too, with the intervention of the coats of the vessels through which the blood circulates. This objection, however, has no real force. Although carbon, in its solid form, requires a high temperature to cause it to combine with oxygen, yet when it makes part of a ternary or quaternary combination, in which its cohesion no longer opposes the combination, it is abstracted, and combined with oxygen at any natural temperature. It is thus that many vegetable and animal substances, when humid, are altered by exposure to the air, and carbonic acid formed. Blood itself is acted upon in this manner. Arterial blood was exposed by Fontana to atmospheric air for three minutes, when no perceptible alteration was occasioned in the purity of the air: they were then agitated together for three minutes: the volume of air was diminished, and its purity impaired. When oxygen gas was substituted for atmospheric air, the alteration was more considerable, its purity being diminished even when agitation was avoided; and when it was agitated, the diminution in purity and volume was still greater. In all these experiments, carbonic acid was produced *. They therefore prove, that oxygen can attract carbon from arterial blood. With venous blood the formation of carbonic acid is, according to Luzuriaga, greater †. If, therefore, oxygen can abstract carbon from the principles of the blood under such circumstances, it is evident it must do so more rapidly during respiration, where the blood is exposed on an extensive surface, and in a state of extreme division, and where that surface, as well as the air itself, are rapidly renewed. The thin membrane which forms the coats of the vessels through which the blood circulates can oppose little obstacle to this reciprocal action. Every humid substance is permeable to elastic fluids, and is penetrated by them. Animal membrane, in a denser state than that which forms the coats of the extreme blood-vessels, is when humid pervious to gases: and what is in point in the present case, through such mem-

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* Opuscules Physiques, p. 334. 335.

† Dissertatio Inauguralis, p. 53. 54.

branes, when humid, oxygen can act on blood, and communicate to it the florid colour. Thus, Priestley found by experiment, that if a quantity of black blood were inclosed in a moistened bladder, which was tied very close, on hanging it in a free exposure to the air, it acquired "a coating of a florid colour, as thick as it would have acquired if it had been immediately exposed to the open air; so that this membrane had been no impediment to the action of the air upon the blood." Mr Hunter mentions a similar experiment, that of covering blood "with gold-beaters' skin, and finding that it became of a florid red on the surface, and even for some depth *." Nor is there any reason to believe, as has been contended, that in the living solids this property is suspended, for it is one connected merely with mechanical structure, and the influence of humidity. The whole action is purely chemical, and the same as that which is exerted between air and blood out of the body, favoured only by the circumstances of exposure, temperature, and agitation, under which it takes place.

It is to be stated as an important fact, independent of all theory, that the changes which take place in respiration are considerably influenced by external circumstances, and by causes which seem to affect the chemical changes of the living system. Crawford found, that less oxygen is consumed by respiration at a high than at a low temperature, a Guinea pig for example not vitiating above half the quantity of oxygen in air in which it was confined at the temperature of 104°, which it did in the same time in air at 55° †. This was confirmed in the experiments of Lavoisier and Seguin ‡; a man consuming, at the temperature of 54°, 1344 cubic inches of oxygen in an hour, while, at the temperature of 79°, he consumed only 1210 cubic inches. De

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* Treatise on the Blood, p. 62.

† Experiments on Animal Heat, p. 307. &c.

‡ Memoires de l'Acad. des Sciences. 1789, p. 575.

la Roche obtained in experiments on different warm-blooded animals the same result [*]. Crawford observed also, that, in an animal placed in a warm medium, the venous blood approaches to the arterial in colour; in a dog, for example, surrounded with water at 114°, for half an hour, at which time the heat of his body had risen from 102° to 109°, the venous blood had assumed so much the hue of arterial, that it was difficult to distinguish between them; and this was confirmed in repeated experiments. It has also been verified by De la Roche. Hence it appears, that the high temperature counteracts those chemical changes which the blood undergoes in the extreme vessels, and the diminution in the consumption of oxygen by respiration, is no doubt owing to this cause. In the series of experiments by Lavoisier and Seguin, was also confirmed, what however had formerly been known, that the consumption of oxygen is influenced by the food and by the state of digestion. During digestion, the consumption of oxygen was increased to 1800 or 1900 cubic inches in an hour. Exercise increased the proportion consumed. It is stated, that Seguin, in continuing the exercise of raising a weight of 15 lbs. to a height of 613 feet during a quarter of an hour, consumed 800 cubic inches, which is at the rate of 3200 in an hour. And the same exercise made during digestion, occasioned a consumption equal to 4600.

In these experiments the result rather singular appeared to be established, that the greater or less proportion of oxygen in the air breathed has little influence on the quantity consumed: whether an animal breathed pure oxygen gas, or mixtures of it with nitrogen gas, the quantity consumed was the same [†]. Lavoisier had even observed, in some of his earlier experiments, that less oxygen is consumed when it is breathed pure; and this also appeared to be established by Davy's experiments, the consumption being only 28 cubic inches in a minute, when, in atmospheric air, it amounted to 31 *, and less carbonic acid being formed. Messrs Allen and Pepys found, however, that in breathing pure oxygen gas, more of it is consumed in a given time, and more carbonic acid formed, than in breathing atmospheric air; they farther found a diminution in the gas respired, whence they considered it as probable, that when oxygen is breathed pure, a portion of it is absorbed; and they found reason to conclude, that there is a similar absorption of oxygen when the same portion of atmospheric air is repeatedly breathed. But in these cases it is difficult to obviate the source of error from the residual air in the lungs, especially when respiration becomes laborious, and the full quantity is not thrown out at the concluding expirations.

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[*] Journal de Physique, tom. lxxvii. p. 1.

[†] Mémoires de l'Acad. des Sciences, 1789, p. 575.

Dr Prout has more lately given an extensive series of experiments †, whence he has inferred certain results with regard to the influence of circumstances which affect the chemical changes in respiration. The proportion he finds in human respiration is not uniform during the 24 hours, but is always greater at one period than another; generally the consumption of oxygen and corresponding production of carbonic acid are at a maximum in the early or middle part of the day, that is, between 10 A. M. and 2. P. M. and decline in the evening and through the night; and whenever the proportion is by any cause increased above the natural standard of the period, it is subsequently as much depressed, and *vice versa*. He farther found, that moderate exercise seemed at first to increase the quantity of carbonic acid, but after being continued for some time, it ceases to produce this effect, and if prolonged so as to induce fatigue, diminishes it. Violent exercise seems to lessen the quantity even at first, and always does so after a short time. The exhilarating passions at first increase the quantity; the depressing passions and anxiety have the reverse effect,—alkohol and all liquors containing it diminish remarkably the quantity of carbonic acid thrown off, and this apparently under all circumstances. The influence of these causes seemed from Dr Prout's experiments to be independent, or nearly so, of their effect on the circulation. How far they are connected with the state of the blood to form carbonic acid, or with that of the organs of respiration, either to form or to discharge it, is a question apparently undetermined. Dr Fyfe has established by experiment some similar results. Wine and alkohol he found to diminish considerably the quantity of carbonic acid; it was also remarkably reduced under the operation of mercury; vegetable diet, after being continued for seven or eight days, caused a diminution; the effect of animal diet was more variable *.

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* Researches, p. 442.

† Annals of Philosophy, vol. ii. and iv.

The phenomena of respiration are nearly the same in all animals: they all require oxygen, and expire carbonic acid; though the quantities are various in the different orders. In warm-blooded animals, the changes proceed to the greatest extent, and the presence of oxygen is most indispensable; and among these, this is in a great measure in proportion to the size of their lungs. In the *amphibia*, the supply of air is less indispensable, as they can sustain the deprivation of it longer; though they still require it, and produce in it the usual changes. Fishes after some time die in water deprived of air, and, according to Priestley, they deteriorate the air contained in the water in which they live †, results confirmed by Spallanzani. Humboldt and Provencal lately investigated this with more precision. Expelling the air from river-water by heat, they found it to contain about 31 *per cent.* of oxygen, with from 4 to 6 *per cent.*, and sometimes even more, of carbonic acid, the remainder being nitrogen. Fishes being confined in a given quantity of this water until their respiration appeared laborious, they were withdrawn, and the air remaining in the water was expelled by ebullition as before. Its proportion of oxygen was diminished to that of seven, nine, or twelve hundredths, and sometimes even to two hundredths of the volume of the air expelled. The quantity of carbonic acid was increased to 22 or 24 *per cent.* of the volume of the residual air *. There appeared to be a consumption of oxygen exceeding that forming the carbonic acid, and also a loss of nitrogen; but this, as Mr Ellis has shewn, may have arisen from fallacies attending the experiment †. The experiments of Vauquelin ‡, as well as the extensive researches of Spallanzani ||, have demonstrated, what had before been more or less accurately observed, that insects and worms consume oxygen, and form carbonic acid, though life in these animals is so languid, and remains so long under the suspension of its usual functions, that they can sustain the deprivation of oxygen for a longer time than animals of the other classes. Spallanzani had observed, that in cold-blooded animals an increase of temperature, contrary to what occurs in warm-blooded animals, increases the chemical changes in respiration; and De la Roche found in experiments on frogs the same result.

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* Dissertatio Inauguralis, 1814.

† Experiments on Air, vol. iii. p. 382.

Connected with respiration, and with the changes which the blood suffers in that process, is the production of animal heat. In the more perfect animals, the temperature of the body is superior to that of the surrounding medium. Thus, in man it is about 96°; and it remains at this, un-

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* Mémoires d'Arcueil, tom. ii. p. 559.

† Farther Inquiries, &c. p. 264.

‡ Annales de Chimie, tom. xii.

|| Memoirs on Respiration.

der exposure to a temperature 40, 50, or 100 degrees lower. It is evident, therefore, that there exists in the system some process causing a constant evolution of caloric, by which this equable and comparatively high temperature is preserved. The action of the air in respiration is demonstrated to be its source; and the view which has been given of this subject, displays the most perfect application of chemistry to physiology, and affords even the most perfect elucidation which we yet have of any function of the living system.

Mayow ascribed the production of animal heat to the action of the air in the lungs; but his opinion, supported by no decisive evidence, was little regarded. Dr Black, observing the analogy between combustion and respiration, particularly that in both processes the air undergoes a similar change; and also observing that in different animals the superiority of their temperature over that of the surrounding medium, is greater the larger their lungs are, and the more air they consume;—that in birds it is higher than in quadrupeds, and in quadrupeds than aquatic animals; drew the conclusion, that respiration is the source of animal heat. It is to Dr Crawford, however, that we are indebted for the theory by which these phenomena are fully explained.

From the changes which take place during respiration in the air in the lungs, Dr Crawford shewed, that caloric must be rendered sensible. Oxygen is consumed, and carbonic acid formed. But we know, that in the formation of carbonic acid from the combination of oxygen with carbon, a large quantity of caloric must be extricated, since the capacity of carbonic acid is inferior to the mean of the capacities of the carbon and of the oxygen gas.

But Crawford at the same time ascertained by experiment, that the capacity of the blood changes when it is converted from arterial to venous, and of course from venous to arterial: the difference between them he found to be as

1.030 to 0.892; that is to say, supposing the capacity of water for caloric to be 1000, the capacity of arterial blood is rather larger, or 1.030, while that of venous blood is considerably less, or only 892.

On these facts he founded his doctrine of animal heat. In respiration, a quantity of oxygen is combined with carbon, so as to form carbonic acid. A quantity of caloric must be extricated in consequence of this. But the blood losing carbon is at the same time changed from venous to arterial, and by this change acquires an increased capacity for caloric. It therefore takes up the caloric which has been extricated by the combination, so that any rise of temperature in the lungs which would be incompatible with life is prevented. The arterial blood is carried, in the course of the circulation, to the extreme vessels, where it passes to the venous state. In this conversion, its capacity for heat is diminished as much as it had been before increased in the lungs: the caloric, therefore, which it had taken up, is again given out; and this slow and constant evolution of heat in the extreme vessels over the whole body, is the source of its uniform superior temperature.

It is this view of the changes of capacity which the blood suffers, which forms the peculiar feature of Crawford's theory. It might easily have been said, that respiration is the source of animal heat; and the observation of a few analogies, such as those stated by Dr Black, might have given probability to the assertion. But the difficulty lay in explaining how this heat, if derived from this source, was not excessive in the lungs, or how it was equally distributed over the body. This is explained from the changes of capacity which the blood suffers in its different states,—changes too, not hypothetically assumed to explain the phenomena, but established by experiment. Yet it is singular how much this has been misunderstood, and how often the objection, which I quote from a modern systematic writer, has been urged by physiologists: " Si la chaleur vital tirait sa source unique des poumons, elle devrait être dans ces organes incomparablement plus forte qu'elle ne l'est par tout ailleurs; et l'activité de cet embrasement, necessaire pour echauffer tout le corps, irait à detruire la substance des parties qui en seraient le foyer *." The very excellence of Crawford's theory is, that it obviates this objection, and accounts satisfactorily for the temperature not being raised in the lungs.

This admirable theory has been confirmed by other experiments, and independent of the direct facts upon which it has been founded. Crawford himself, and afterwards Lavoisier and La Place, found, that, when an animal is confined in a vessel contrived so as to measure the quantity of caloric which it gives to the surrounding medium in a certain time, and the quantity of oxygen consumed by the animal in that time, the quantity of caloric corresponds nearly to the quantity evolved from the combustion of carbonaceous matter, such as wax or oil, in the same quantity of oxygen. It has been found, too, that whatever increases the heat of the body, such as violent exercise, or, in general, whatever augments the circulation, increases the consumption of oxygen in the lungs.

Some experiments have been stated, in which it has been alleged, that there is little or no difference in the capacities of arterial and venous blood. But they are not of such a nature as to invalidate the experimental results of Crawford, or the principles on which his explanation of animal heat is founded.

The theory of Crawford has also been impugned on other grounds. In a series of experiments by Mr Brodie †, artificial respiration was produced by the inflation of the lungs in animals newly killed by narcotic poisons, or division of the spinal marrow, and in whom the motions of the

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* Dumas, Principes de Physiologie, tom. iii. p. 555.

† Philosophical Transactions, 1811, 1812.

heart, and of course the circulation, had not ceased. By keeping up artificial respiration, these could be continued. It was found, that the usual chemical changes in the lungs were thus carried on; oxygen gas was consumed and carbonic acid formed. The conversion of venous into arterial blood was also apparently effected, the usual change of colour taking place. But the temperature of the animal fell. In the first experiment for example, on a rabbit, the temperature fell in half an hour from 97° to 90°; and in a number of trials there was a similar result. Heat, therefore, it was concluded, had ceased to be generated, though the usual changes supposed in the theory of Crawford to be the source of its production in the animal body were carrying on; hence it seemed to follow, that these changes are not the real source of animal temperature,—that therefore, as Mr Brodie inferred, the theory is not just; and farther, as the nervous energy had in these cases ceased to operate, though the circulating and respiratory functions were in action, "that the temperature of warm-blooded animals is considerably under the influence of the nervous system." Some facts from morbid cases, particularly of paralytic limbs, where heat was deficient, though the circulation through the limb was perfect, had been before brought forward as grounds of a similar argument.

There are fallacies attending these experiments in the estimation of the comparative changes in artificial and in natural respiration, which it must have been very difficult to obviate entirely. But independent of these, there is an important error affecting the result, the correction for which altogether invalidates the conclusion which was drawn, that heat had not been generated. If it had not, the temperature should have been reduced more rapidly, and to a greater extent than it actually was, and of course the opposite conclusion follows, that heat was produced. In each experiment, while the animal subjected to it was under the influence of artificial respiration, by air being forced into the lungs, another animal of the same species and size killed at the same time, was placed under a similar vessel, but without artificial respiration, so that the fall of its temperature might be compared with that in the other. The difference was in general inconsiderable. In the first experiment, for example, the temperature of the animal subjected to artificial respiration had fallen in 30 minutes from 97° to 90°, that of the other in the same time from 97° to 91°: and in other experiments the differences were the same, or even less. Now in the former animal, during the whole period, air was forced into the lungs, and withdrawn at the rate, as is mentioned, of about 50 inflations of the lungs, or from 50 to 60 in a minute, and to this air thus constantly renewed, and in the interval exposed to the cooling agency of a glass vessel of the capacity of 500 cubic inches, the bulk of the animal itself being 50 cubic inches, the whole mass of blood circulating through the lungs was exposed, by which it must necessarily have been constantly cooled. The artificial respiration would at the same time abstract a constant portion of watery vapour from the lungs, the formation of which equally caused an expenditure of heat. Yet notwithstanding these sources of the constant abstraction of heat, the fall of temperature at the end of 30 minutes was not greater than 1 degree, or half a degree more than where they were not present, a proof sufficient that heat must have been generated, and probably to as great an extent as is to be looked for from the chemical changes which actually took place.

As the temperature did fall however, the heat generated, it might be inferred, is not equal to that from natural respiration. To establish this, the comparative extent of the changes would require to be accurately determined. The abstraction, for example, of a little more watery vapour from the lungs in the artificial respiration, than what is discharged in the natural respiration, a circumstance very likely to have occurred, from the mode in which the experiment was performed, would be sufficient to give rise to this result. And even admitting that the heat evolved is not so great in the one case as in the other, there is no reason to infer that it should be equal. It is not sufficient to establish this conclusion, to shew that the usual chemical changes go on in the lungs; it is not less necessary to prove that the corresponding changes producing evolution of heat take place in the extreme vessels, a proof which it is apparently impracticable to give. It is quite possible, that the blood in the course of the circulation may lose its florid colour, and yet, under that state of the system in which nearly all the functions are suspended, may not become proper venous blood, to that extent as to suffer the full diminution of capacity which is necessary to maintain the standard temperature; and this blood may for a long period afford carbon to form carbonic acid when acted on by the air in the lungs, and from this change may suffer augmentation of capacity, so that its temperature shall not rise;—these changes arising from the mere chemical action of the air on the blood, unconnected with the exercise of any vital function in the extreme vessels. Caloric, therefore, may be communicated to the blood in the lungs, to all the extent to which it is necessary to suppose it communicated in these experiments, and yet neither raise its temperature, nor be evolved in the extreme vessels, under the circumstances in which the experiments were performed; and this too without the conclusion following, that the blood should suffer any change of properties incompatible with the operation going on, as long as the experiment could be continued.

To say that nervous energy is the source of animal heat, amounts to nothing precise. As the temperature of animals is superior to that of the medium in which they live, there is not only an evolution of heat to produce that superior temperature, but there is a still greater evolution necessary to supply that constant abstraction of it which is imparted to the surrounding medium. Caloric must therefore be supplied from some external source, and though the state of vitality may modify the chemical processes in the system by which heat is evolved, it can with no precision be said to be the source of heat, nor is any thing gained by saying that the generation of heat depends on its influence. In respiration the air suffers changes which we know in all other cases are accompanied with an evolution of caloric, and the theory of Crawford shews how these give rise to the phenomena of animal heat; we have the additional evidence, that the superior temperature of animals is proportional to the quantity of oxygen they consume in respiration, and that the heat evolved by an animal is almost precisely the same as that evolved by the consumption of the same quantity of oxygen in other cases where carbonic acid is formed. With such proofs, we can scarcely hesitate in admitting the conclusion conformable to this theory,—that the chemical changes which occur in respiration, with the corresponding changes in the extreme vessels, are the source of animal temperature[*].

When an animal is placed in a medium, the temperature of which is considerably high, it still preserves its temperature for a time at least nearly uniform; the animal heat not rising much above the natural standard, as has been demonstrated by the experiments of Tillet[†], and of Fordyce and Blagden[‡]. In those of the latter, air was breathed at a temperature of 212°, and even 260°; and in some cases reported by the former, an exposure to an atmosphere of 250° was sustained for 15 minutes, and to an air of 280° for 10 minutes. In this case of confinement in a heated atmosphere, it has been ascertained by the experiments of Crawford, that the usual change of arterial into venous blood does not go on, the blood in the veins being nearly as florid as in the arteries. It is evident, therefore, that no evolution of caloric will take place; and it is even possible, that the temperature of the body may be kept low by the blood acquiring an increased capacity for caloric, though other circumstances, particularly the imperfect conducting power of the animal solids, and the increased perspiration, with the evaporation from the surface, have a share in the effect. Dr De la Roche has in particular shewn, that the loss of weight from the profuse perspiration is very considerable, even in not many minutes; and has found reason to conclude from experiment, that the consequent evaporation is the cause counteracting increase of heat *.

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[*] A series of experiments in prosecution of this subject, has been recently made by Legallois, a French physiologist, (Annales de Chimie et Physique, tom. iv.). They scarcely lead to any certain results, while the cruelty of the whole investigation, more especially in these last experiments, is revolting, and could scarcely be palliated by the importance of any conclusion that could be drawn.

[†] Mémoires de l'Acad. des Sciences, tom. xxxiii. p. 522.

[‡] Philosophical Transactions, 1775.

TRANSPIRATION is a function analogous to respiration, and has been believed to produce the same chemical changes in the air. There is also an exhalation of aqueous vapour, which, augmented by heat or exercise, is condensed on the surface, and forms the sweat. De Milly observed, that when the hand is kept in warm water, carbonic acid gas is disengaged from the surface. The same fact was established by Cruickshank †. But as the air applied to the hand was confined by a moistened bladder, they were liable to the fallacy that the bladder might be acted on by the oxygen, and afford this carbonic acid. The production of carbonic acid, as well as the consumption of oxygen, seemed to be established, however, in a more unequivocal man-

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* Nicholson's Journal, vol. xvii. p. 215. xxxi. p. 561.

† Cruickshank on Insensible Perspiration.

ner by Abernethy and Jurine. The former exposed his hand to seven ounce-measures of atmospheric air confined over mercury, for five hours; at the end of that time the air had diminished in volume half an ounce measure, and by agitation with lime-water, one ounce more was absorbed, the lime-water being rendered milky; the residual air contained one-sixth less oxygen than before the experiment *. Jurine found, that on fixing bottles containing atmospheric air to the surface of the skin, the air was vitiated, diminished in volume, and contained carbonic acid †. These changes in the air are also accompanied with the exhalation of watery vapour. Cruickshank, by inclosing his hand in a glass vessel, the orifice of which was secured at the wrist with a bladder, observed that the glass became dim, and drops of water were condensed on its surface. In this way about 30 grains of water were collected in an hour, though on repeating the experiment the quantity was sometimes much less, and at other times, especially after exercise, was greater ‡. From these facts it appeared, that the skin performs functions, with regard to the atmosphere, the same as those performed by the lungs. But they have been considered as doubtful. Priestley had found some uncertainty in the results; and Dr Klapp, repeating the experiments of Abernethy, did not find any emanation of carbonic acid gas, nor any change to be produced in the air in which the hand was confined, either when atmospheric air or oxygen gas was employed, though the experiment was continued for several hours ||. Mr Ellis has reported some experiments made by Dr Gordon with the same results; but he adds some experiments posterior to these, made by Dr C. Mackenzie, in which car-

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* Physiological Essays, p. 118.

† Mémoires de la Sociéte de Medicine, tom. x.

‡ Experiments on Insensible Perspiration, p. 69. &c.

|| Treatise on the Functions of the Skin.

bonic acid was detected in air that had been kept in contact with the skin for two hours*. Spallanzani concluded from his experiments, that a number of animals of the lower classes, serpents, frogs, insects, and zoophytes, produce the same changes on the air by their skin as are produced by the respiratory organs †.

Lavoisier and Seguin endeavoured to determine what proportion the changes by transpiration bear to those by respiration ‡. They employed a covering of silk rendered air-tight by being coated with a varnish of caoutchouc, and adapted to the body, so that the products by the skin could be separated from those by the lungs. By taking the weight, before entering the apparatus and after leaving it, the whole loss of weight in a given period could be ascertained; and by weighing a few moments after being inclosed in the apparatus, and a few moments before withdrawing from it, the loss of weight from respiration alone was determined, and thus the proportion by each process could be established. The following are the results: The loss of weight sustained by an individual, not under any unusual bodily labour, varies from 11 grains in a minute to 32, or in twenty-four hours from 1 lb. 11 ounces 4 drachms, to 5 lbs.; this including the effects from transpiration and respiration. The mean loss is 18 grains each minute, 1 ounce 7 drachms an hour, or 2 lbs. 13 ounces in twenty-four hours; and in separating the effects of each of these functions, of these 2 lbs. 13 ounces, there belong to cutaneous transpiration 1 lb. 14 ounces, and to respiration 15 ounces. These results can be regarded only as approximations: the uncertainty of those which relate to respiration have been already noticed; and with regard to the effects from transpiration, it appears from the account given by Seguin, that the watery product only had been attended to, and that there had been no estimate of the oxygen consumed, or carbonic acid exhaled by the skin, if any such changes did occur.

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* Farther Inquiries, &c. p. 554.

† Rapports de l'air avec les eteres organises.

‡ Mémoires de l'Acad. des Sciences, 1790, p. 601.

The skin appears to secrete a small portion of acid, as it sometimes is capable of communicating to the more delicate vegetable colours a red tinge, and distilled water rubbed on it is rendered turbid by nitrate of silver. When this secretion of fluid is more copious, it is sensibly acid. The free acid contained in sweat is acetic according to Thenard, according to Berzelius lactic; with this are present, muriate of soda, and minute traces of phosphate of lime, and oxide of iron, with a little animal matter *.

SECT. II.—OF THE CHYLE.

THE food digested in the stomach, passes into the intestinal canal; and in its progress, there is separated from it by the absorbents which terminate on the internal surface of the canal, a white liquor, which is conveyed to the thoracic duct, and ultimately into the blood. This is the Chyle,—a fluid, the composition of which is important, as it is from it the blood is formed, and by its medium nutrition is conveyed. From the difficulty of procuring it, it had not been much examined; but lately it has been the subject of investigation by Vauquelin †, Brande ‡, and Marcet ||.

Its colour is white; its taste is sweet, and slightly saline; but these qualities vary according to the time at which it

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* Nicholson's Journal, vol. xix. p. 66.

† Annals of Philosophy, vol. ii. p. 220.

‡ Philosophical Transactions, 1812.

|| Medico-Chirurgical Transactions, vol. vi.

is taken after food has been received : about four hours after food has been taken, it appears to be most perfect. It does not affect the colour of litmus or turmeric, but slowly changes that of violets to a green. After standing for some time, 10 or 15 minutes, it assumes a gelatinous appearance ; and it gradually separates into two parts, one a coagulum, the other a liquid. This change is evidently similar to the coagulation of blood, and is promoted and retarded by the same causes, the coagulum only being less firm. It affords the simplest analysis to discover the composition of chyle.

The coagulum is white, with very frequently a pink hue; sometimes semi-transparent, at other times opaque ; it has a slight degree of elasticity, and is slightly fibrous : it is rapidly dissolved by the alkalis ; the solutions by potash and soda exhale a little ammonia ; the solution by ammonia is of a reddish colour. Acids added to these solutions precipitate a substance which, Mr Brande remarks, is intermediate between fat and albumen : nitric acid in excess dissolves it in the cold, and sulphuric, muriatic, and acetic, with the aid of heat. Alkohol and ether dissolve a small portion of this precipitate, which has the properties of spermaceti ; the remainder appears to be coagulated albumen. The different acids act differently on the pure coagulum. Sulphuric acid diluted with an equal weight of water dissolves it, and with the aid of heat does so even in a state of greater dilution, forming a liquor of a brown colour, from which the alkalis throw down no precipitate. Nitric acid diluted with three of water dissolves a portion of it, and leaves a matter analogous to gelatin ; if more diluted it converts it slowly into adipocire. Muriatic acid concentrated does not dissolve it, but when diluted with an equal weight of water, forms a yellowish solution. Acetic acid boiled upon it dissolves a small portion, which after cooling is deposited in flakes having the properties of coagulated albamen. Subjected to destructive distillation, the coagulum affords the usual products of animal matter; and the residual charcoal by incineration yields a considerable portion of muriate of soda and phosphate of lime, with very slight traces of iron. This substance seems in several of its properties analogous to albumen, in others to fibrin. It seems, says Vauquelin, to be albumen which has begun to assume the characters of fibrin, as it combines several properties common to both.

The fluid which separates from the coagulum of chyle is, when the coagulation has been complete, transparent and colourless; when imperfect, it is turbid and sometimes white; its quantity at first is about two-thirds of the chyle, but a quantity in addition to this remains in the coagulum, which gradually oozes out. According to Vauquelin, it restores the blue colour to litmus reddened by acids, proving the presence of a free alkali. When heated it becomes turbid and milky, and, according to Brande, deposites flakes of albumen. Alkohol likewise causes an abundant coagulation in it; the coagulation is white, when dry, transparent, and is dissolved by potash. The mineral acids, if not too much diluted, also coagulate it, and throw down an abundant precipitate of albumen, which is re-dissolved by alkaline solutions. This albumen, Vauquelin remarks, constitutes the greater part of the solid matter of chyle. Along with it there seems to be a portion of oily or fatty matter, for when the albumen is separated by the addition of warm alkohol, Vauquelin found that a small portion is retained in solution, which is partly separated in cooling; and is partly held dissolved, so that the addition of water causes milkiness; and the alkaline solution of the precipitate by acids remains, from the presence of the same matter, white and turbid, instead of being transparent, as that of pure albumen is. By evaporation of the alkoholic solution, Vauquelin obtained it in the state of an oily concrete matter, and he regards it as analogous to the fatty matter of the brain, particularly in the character of being imperfectly soluble in alkohol. A portion of the same substance he found to be contained in the coagulum. It is no doubt this matter which gives to chyle its milky appearance, more or less according to its quantity. Dr Marcet observed, that from the serous portion of the chyle furnished by animal food, an opaque creamy substance separated on standing, and collected on the surface; and this substance assumes the consistence of butter. Vauquelin, in the chyle of the horse, in one case found, that the milky fluid which surrounded the coagulum was partly covered with drops of a yellowish oil. The same facts had been observed by others. One other principle appears to exist in the serous fluid of chyle. When, after the separation of its albumen by heat, it is evaporated to half its bulk at a temperature not exceeding 200°, small crystals were observed by Mr Brande to separate on cooling, which had a strong resemblance to sugar of milk; they required for their solution 4 parts of boiling water, and from 16 to 20 of cold water; are sparingly soluble in boiling alkohol; the taste of their watery solution is extremely sweet, and by nitric acid they are converted into a white powder of sparing solubility, having the properties of the acid of sugar of milk. The destructive distillation of the whole serous part of chyle afforded to Mr Brande a minute quantity of charcoal, yielding traces of phosphate of lime, and muriate and carbonate of soda. Vauquelin states as the products of the incineration of chyle coagulated by heat,—carbonate, muriate, and sulphate of potash, iron, and phosphate of lime: muriate of soda, it has already been stated, is obtained from the burnt coagulum in considerable proportion.

Dr Marcet found some differences in the chyle of the dog from animal and from vegetable food. The former was more thick and opaque, nearly like cream; the serum on standing afforded a cream, and it was rendered more turbid from the separation of albumen by heat; and the coagulum was less transparent, and of a more distinct pink hue.

Chyle has evidently an analogy to blood, more especially in its spontaneous coagulation. As the coagulum acquires a reddish tint from exposure to the air, it may be inferred, that this fluid acquires the red colour which will complete its conversion into blood, by the action of the air in the lungs.

Different results have been obtained from experiments on the effect of substances introduced into the stomach, on the composition and properties of the chyle. Colouring matter mixed with the food, appears sometimes to communicate to it a tinge, sometimes not. According to Lister, it receives a blue colour from indigo received into the stomach ; an observation confirmed by Haller, who did not find, however, any effect from other substances, which had been said to give it colour. Dr Fordyce also observed, that indigo thrown into the intestines renders the chyle blue, and that musk communicates to it a strong odour. This intermixture of substances, however, conveyed by the stomach, does not always happen. It has been found, that when iron is mixed with the food, no traces of it are to be discovered, by the test of infusion of galls, in the chyle *; and this has been stated as an argument to prove that iron is not derived from without, but is formed in the animal system.

THE CHYME is the soft pulpy mass into which the food has been resolved by the process of digestion in the stomach, and from which the chyle is prepared. It must vary according to the nature of the food, and the perfection of digestion. Dr Marcet found it, as procured from the stomach of a turkey, to be a homogeneous brownish

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* Fordyce on Digestion, p. 122.

pulp, neither decidedly acid nor alkaline, though inclining to the former, and not very liable to putrefaction. It contained albumen; and by evaporation to dryness, afforded one-fifth of its weight of solid matter, which by incineration afforded a charcoal containing various saline substances, among which the presence of iron, lime, and an alkaline muriate, could be ascertained.

SECT. III.—OF MILK. SUGAR OF MILK. SACCHO-LACTIC ACID.

MILK is the fluid designed for the nourishment of young animals, and is secreted by a particular glandular apparatus in the mammæ of the female. It differs in its sensible qualities in different animals, but its chemical properties appear to be nearly the same. These have been often the subject of investigation. Besides the knowledge of it received from the older chemists, an elaborate examination of it was undertaken by Parmentier and Deyeux *, and some facts have been added by Lagrange †, and Berzelius ‡.

Milk is white and opaque, its taste is bland and sweet, its smell faint; its consistence is somewhat thick, and its specific gravity a little greater than that of water. These qualities vary, however, not only in different animals, but according to the diet and state of the digestive organs.

When milk newly drawn is allowed to remain at rest, it suffers a slight spontaneous decomposition, a thick bland fluid collects on the surface, and the liquid beneath is more watery. This change has been ascribed to the action of the air. Young asserted, that it takes place equally when

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* Expériences sur le Lait.

† Nicholson's Journal, vol. x. p. 141.

‡ Medico-Chirurgical Transactions, vol. iii.

the air is excluded,—an observation since confirmed by Thenard. This seems indeed more probable, since, from the opacity of milk, it is obvious that an oily fluid is diffused through a watery one, and white globules are even discovered in it by the microscope. It is these that separate spontaneously when the milk is at rest, and form the cream.

The Cream is a substance of an oily nature, and when agitated for some time, separates into a fluid and a solid part, the latter having the properties of a concrete oil. This oily substance, or Butter, is the first proximate principle which a simple analysis discovers in the milk. It is bland and sweet, but becomes rancid on exposure to the air. By distillation, it is converted principally into a fluid oil, and, when decomposed by heat, affords the same products as animal fat. The cream is a mixture of this oily matter with the cheese and whey, which form the other parts of the milk. According to Berzelius, the separation of butter from it by agitation is accompanied with an absorption of oxygen, whence the production of acid.

After the separation of the cream, the milk begins to suffer another change, which is more rapid in a high than low temperature. It becomes acescent, and then coagulates. When this coagulum is pressed gently, a serous fluid is forced out, and a solid matter, somewhat elastic, and insoluble in water, remains. This is the caseous part of milk, or the pure Cheese.

This change appears to be owing to the formation of a small quantity of acid in the milk, which re-acting upon it, separates the caseous matter; and, according to Thenard, a portion of the acid combines with the cheese, though with an attraction so weak, that it may be removed by washing with water. Acids, accordingly, added to milk, even though very weak, immediately coagulate it: many other substances have the same effect, as several compound salts, especially those containing an excess of acid, alkohol, sugar, gum, the gastric juice of animals, and the juices of several vegetables. This caseous matter is also separated by heat. If milk be heated in contact with the air, a thin pellicle forms upon its surface: and if this be removed, a new one is formed. After the formation of these has ceased, the remaining fluid is thin and serous. Parmentier and Deyeux have ascertained, that these pellicles consist of a matter identical with cheese. Its separation from the milk is promoted by the contact of the air, but apparently merely by its mechanical action, and not by any chemical effect; since its separation they found to be equally promoted by oxygen, hydrogen, or carbonic acid gas.

The coagulum separated by these substances is nearly the same in its properties. The liquor found in the stomach of young animals, what is termed Rennet, is preferable to obtain its full separation. The curd formed by adding it to milk moderately heated, is the caseous matter retaining a portion of the serum or whey, which can be easily separated by pressure. The coagulating power of the rennet was ascribed to a portion of acid which it contained; but Young, and Parmentier and Deyeux, have shewn, that it is the property of the juice itself, since, even when an alkali is added to it in excess, it retains the coagulating power. The membrane of which the stomach is composed likewise possesses this property, and communicates it to water macerated upon it. The cause of the coagulation is not well understood.

The Caseous matter of milk is a white or greyish substance, somewhat elastic: when fresh, it is nearly insipid, but becomes acrid on keeping. It is insoluble in cold water, but by boiling its texture is destroyed. If exposed in a moist state to the air, it soon putrefies. If the moisture has been pressed out of it, and if it has been dried by a gentle heat, it remains long unchanged.

The fixed alkalis, dissolved in water, and assisted by a moderate heat, act upon the caseous matter readily. It is dissolved, and ammonia is exhaled, probably formed by the combination of its elements. If an acid is added to the solution, a precipitate of a dark red colour is thrown down, and a smell of sulphuretted hydrogen is perceived. Silver is blackened by the liquor in a short time. Ammonia is likewise capable of dissolving the caseous matter.

The mineral acids, when diluted with water, effect a solution of it, but not completely. The vegetable acids, particularly vinegar, dissolve it entirely, and with more facility. Nitric acid disengages from it nitrogen gas.

The caseous matter decomposed by heat affords an empyreumatic oil, ammonia, and a species of carburetted hydrogen. A residuum of charcoal is obtained, which, when burnt, affords, as Scheele ascertained, a portion of phosphate of lime. It contains, as Berzelius has remarked, neither alkali nor oxide of iron. The proportions of its elements, ascertained by Gay Lussac and Thenard, are given in the table at the end of the preceding chapter.

The pure caseous matter must be admitted as a principle differing in some respects from any other animal product. It is most analogous to albumen, as it is soluble in a fluid resembling the serum of the blood, and is coagulated by heat. In several other properties, it is analogous to fibrin. It is the most animalized product of the milk, and is that which is most nutritious. The earthy phosphates obtained by its incineration, it is stated by Berzelius, pre-exist in it, and may be obtained by solution in muriatic acid: and their presence, he remarks, adapts it to the nourishment of the young, in the rapid progress of ossification which the first period of life requires *.

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* It appears that a matter analogous to the caseous or albuminous principle of milk, exists in a number of vegetables. Some seeds and fruits abounding in oil, such as the almond, were known, by trituration with water, to form a liquor, named an Emulsion, si-

When these two principles, the butter and the cheese, have been separated from the milk, there remains a liquor named the Serum or Whey. The composition of this is lastly to be noticed.

The whey has a yellowish colour and slight tenacity: its taste is bland and agreeable. It contains a portion of caseous matter, which is separated by allowing it to stand in a warm place for some hours: it then becomes acescent, the cheese separates in filaments, and, by filtration, the whey becomes transparent.

When this pure whey is subjected to evaporation, it affords a substance of a granulated saline appearance, a sweet taste and yellowish colour, which, by solution and evaporation, yields white rhomboidal crystals. This, which is the principal solid matter in the whey, is named the Salt or Sugar of Milk. In some countries, particularly in Switzerland, it is prepared in considerable quantity.

This substance is soluble in seven parts of cold, and four of boiling water; or, according to Vogel and Lagrange, in five parts of cold water, and boiling water dissolves twice its weight, the greater part of which separates on cooling in small crystals. It is not soluble in alkohol or ether; and alkohol precipitates it slowly from its concentrated watery solution. It is softened, fused, and decomposed by heat; it burns also, but less rapidly than sugar, and leaves more charcoal. In its decomposition by heat, it affords

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milar in appearance to milk,—a result which was supposed owing to the oil being diffused in water by mucilage, fecula, and saccharine matter in the seed. But Vogel and Boullay have shewn, that the almond contains no fecula, but a principle analogous to the albumen or cheese of milk, with a little gum and sugar in addition to the oil; and that the almond emulsion is very similar in its nature to animal milk. It accordingly displays nearly the same chemical properties, (Annals of Philosophy, vol. xi. p. 426. 428.).

products nearly the same as those yielded by vegetable saccharine matter, water, acetic acid, empyreumatic oil, carbonic acid and carburetted hydrogen gases, with a residual charcoal, which by incineration yields, according to Vogel and Lagrange, sulphate, carbonate, and phosphate of lime. From its analysis by the action of hyper-oxymuriate of potash, Gay Lussac and Thenard have inferred, that it consists of carbon 38.825, oxygen 53.834, and hydrogen 7.341. Berzelius, by a similar analysis operating on it, freed from its water of crystallization by exposure to a heat of 212° in a vacuum, obtained as the proportions, carbon 39.474, oxygen 53.359, hydrogen 7.167. But he supposed it to contain combined water, and therefore submitted it to analysis, in combination with oxide of lead, by which this was abstracted; and from the results of this and other methods, he assigned as the proportions, carbon 45.267, oxygen 48.348, hydrogen 6.385 [*]. Sugar of milk may contain a portion of water, for it yields a considerable quantity when heated, without any apparent decomposition. But what the real quantity is, is uncertain, and the composition therefore is imperfectly determined.

The acids either dissolve or decompose sugar of milk. Acetic acid dissolves it simply, as does also liquid muriatic acid; muriatic acid gas combines with it slowly, forming a grey powder; oxymuriatic gas decomposes it slowly, forming water and carbonic acid; nitric acid diluted and in small quantity converts it into a saccharine matter, soluble in water. Potash acts on it with more energy than on almost any vegetable or animal substance. When a little potash is mixed with sugar of milk, on adding a small quantity of water, there is an immediate solution with heat and effervescence; the liquor becomes of a deep brown, and by evaporation affords a soft deliquescent substance of the same colour, analogous to extract, water, carbonic acid, and acetic acid being also formed *. There is a tendency in sugar of milk to this kind of decomposition by alkaline bases.

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[*] Annals of Philosophy, vol. v. p. 266.

When the sugar of milk is treated with nitric acid, assisted by a moderate heat, nitrous gas is discharged, the solution becomes yellow, and, as it advances, a deposition of a white matter takes place. The fluid, when poured off, affords by evaporation crystals of oxalic acid. The white matter obtained in this operation is a peculiar acid. Scheele, who discovered it, gave it the name of Acid of Sugar of Milk: it is named Saccho-lactic Acid. From 16 ounces of sugar of milk, submitted to the action of three times its weight of nitric acid, of the specific gravity of 1.28, there are obtained, according to Trommsdorff, 4 ounces of saccho-lactic with 2 ounces of oxalic acid †.

Scheele supposed that the sugar of milk is a compound of this substance and saccharine matter, and that it is merely rendered sensible by the saccharine matter being oxygenated by the nitric acid. Parmentier and Deyeux accede to this opinion. They observe, that in the process in which it is obtained, very little of the nitrous acid is decomposed, and that, if the quantity decomposed be compared with the quantity of oxalic acid formed, the proportions will be found nearly the same as when oxalic acid is procured by the oxygenation of pure sugar. And they add the synthetic proof, that when two parts of saccho-lactic acid are mixed with one of sugar, a compound similar to the sugar of milk is formed. The opinion, however, as is justly observed by Fourcroy, does not well accord with the properties of these two substances; it is also rendered improbable from the circumstance, that the same acid is form-

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* Memoir by Vogel and Lagrange, Journal de Physique, tom. lxxii. p. 208.

† Nicholson's Journal, vol. xxvi. p. 142.

ed in the action of nitric acid on other substances, as gum, in which there are no grounds for supposing the previous existence of sugar of milk.

Vogel and Lagrange have accordingly submitted again to examination the evidence on which it rests. They found, that the synthetic experiment stated by Parmentier and Deyeux never succeeded: in whatever proportion the saccho-lactic acid and sugar were mixed no compound is formed analogous to sugar of milk, nor could the two substances be brought into chemical combination. Sugar of milk, therefore, is apparently a principle of definite composition, analogous to, but still different from vegetable sugar. It had been affirmed, that it is capable of the vinous fermentation, but Vogel and Lagrange found, that when mixed with yeast, and kept in the proper temperature, there is no disengagement of gas, and though the liquor had a slight smell of alkohol, none could be procured from it by distillation.

Saccho-lactic acid is in the form of a white powder, a little granulated: its taste is slightly sour: it is sparingly soluble in water, 60 parts of boiling water being requisite, according to Scheele, to dissolve it: this solution has an acid taste, and reddens the vegetable colours: it deposites, on cooling, small crystals. At the temperature of 212°, it decomposes the alkaline carbonates, disengaging the carbonic acid. Exposed to heat in close vessels, it is decomposed, the products being an acid liquor, which deposites needle-like crystals, an empyreumatic dark-coloured oil, carbonic acid and carburetted hydrogen gases, and a large residuum of charcoal. According to Trommsdorff, the acid which sublimes is analogous to the succinic acid; and the liquid acid is similar to the pyro-tartaric.

Gay Lussac and Thenard gave as the composition of this acid, carbon 33.69, oxygen 62.69, hydrogen 3.62. Berzelius, from the products of the combustion of the acid, gives as the proportions 31.9 of carbon, 62.84 of oxygen, and 5.26 of hydrogen; and from the analysis by the medium of saccholate of lead, carbon 33.43, oxygen 61.465, hydrogen 5.105 *, which, except in the quantity of the last element, coincides nearly with the results of Gay Lussac. The relation of the oxygen to the carbon, is not that of any of the definite proportions, but is nighest to what may be considered as the third. The hydrogen is in that proportion which constitutes super-carburetted hydrogen.

This acid combines with the different salifiable bases, forming salts named Saccholates; we have no knowledge of these combinations, except from a few observations by Scheele. It forms with potash a salt soluble in eight parts of warm water, which crystallizes on cooling; and with soda a salt equally crystallizable, requiring only five parts for its solution. Both these salts are more soluble, from an excess either of acid or of base. Saccholate of ammonia is easily decomposed by heat, the ammonia being expelled. The compounds with lime, barytes, and magnesia, are nearly insoluble; hence this acid decomposes the soluble salts of these earths. It acts feebly on the metals; and with their oxides, forms salts of sparing solubility. It precipitates the nitrates of silver, quicksilver, and lead.

This acid is formed, not only from sugar of milk, but likewise from gum, by the action of nitric acid: two parts of the acid being slightly heated on one part of gum, until a small quantity of nitric oxide and carbonic acid is disengaged: on cooling, the liquid deposites the saccho-lactic acid; the quantity, according to Fourcroy and Vauquelin, being from 14 to 26 parts, from 100 of gum. From this production of it from mucilage or gum, some chemists name it Mucous Acid. Laugier has shewn, that, as produced by this process, it is contaminated with a portion of oxalate of

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* Annals of Philosophy, vol. v. p. 180.

lime, derived from the combination of oxalic acid formed in the process with lime contained in the gum. This may be abstracted by repeated digestions in dilute nitric acid.*

From the quantity of saccharine matter which milk contains, whey is susceptible of acetous fermentation; and by the Tartar tribes, even a vinous liquor is prepared from mare's milk. The process has been described by Dr Guthrie.† It is extremely weak, eight pints affording on distillation only four ounces of alkohol. Vogel and Lagrange confirmed this fact by experiment, but at the same time they found, that the milk of the cow is incapable of the vinous fermentation. As the sugar of milk is so also, the milk of the mare seems from this to contain a small portion of pure sugar.

Whey passes more readily into the acetous fermentation; it soon becomes acescent, and the acid produced was supposed to be the acetic. Scheele first examined it, and although he observed an analogy to the acetic acid, both in its properties and combinations, he found also some differences between them. He was also unable to obtain it pure by distillation; for although an acid liquor distilled over, this could not be carried far, as a decomposition and a deposition of carbonaceous matter took place from the heat applied. And lastly, it appeared, that this acid decomposed the acetates. Hence he regarded it as different from the acetic; and in the new nomenclature it received the name of Lactic Acid. Lagrange, and Fourcroy and Vauquelin, inferred, however, from experiments, that it is merely the acetic, disguised by a portion of extractive matter united with it, and by the saline substances contained in the whey‡. The latter chemists, in particular, on saturating the acid from sour milk, with an alkali, and decomposing the salt by sulphuric acid, obtained by distillation only weak acetic acid. But Berzelius has remarked, that in such a process the lactic acid would be decomposed, as Scheele had shewn, and converted into the acetic; and from an investigation of its properties and combinations *, he has inferred, that the opinion of Scheele with regard to it is just.

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* Nicholson's Journal, vol. xxviii. p. 14.

† Edinburgh Philosophical Transactions, vol. ii.

‡ Nicholson's Journal, vol. x. p. 264.

Berzelius procured it by digesting dry whey with alkohol, and adding to the liquor a fresh portion of alkohol, to which $\frac{1}{75}$ of sulphuric acid had been added. Sulphate of potash was deposited from the decomposition of muriate of potash; and there remained in the liquid lactic, sulphuric, muriatic, and a minute portion of phosphoric acid. The three latter acids were abstracted by digestion with carbonate of lead, while the lactic acid forms with this, a salt soluble in alkohol. From this solution the oxide of lead was abstracted by sulphuretted hydrogen, and the liquor by evaporation was reduced to the consistence of a thick varnish, of a dark brown colour and acid taste. To free this from animal matter, and from all muriatic acid, it was digested first with lime, and then a portion of it decomposed by oxalic acid; the lactic acid procured from this was by carbonate of silver converted into lactate of silver, this lactate of silver was employed to remove all muriatic acid from the remaining lactate of lime, which was then decomposed by oxalic acid, and the lactic acid was freed by solution in alkohol from any adhering oxalate of lime. It was then supposed to be obtained pure. It formed a clear transparent fluid, of a brownish yellow colour, with a sharp sour taste, without smell in the cold, but emitting a sour smell when heated, incapable of crystallization, and drying into a thick smooth varnish, without any saline appearance, which slowly attracts moisture from the air. It is easily soluble in alkohol. Heated, it boils, exhales a va-

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* Philosophical Magazine, vol. xli. p. 241.

pour, having a pungent acid smell, different from that of acetic acid, and is charred. Distilled, it yields water, empyreumatic oil and vinegar, carbonic acid, and inflammable gases. It forms salts with alkalis, earths, and metallic oxides, which in general are distinguished by being soluble in alkohol, and having no disposition to crystallize, but drying into a mass like gum, which becomes moist in the air. When decomposed by sulphuric acid, they give no smell of acetic acid, and they are altogether different in their specific properties, from those of the acetic, malic, or any other known acid. It is this acid combined with soda, and with an animal matter, which may be separated by means of tannin, which, according to Berzelius, forms the deliquescent extractive matter, which is left after the alkoholic solution from the analysis of many of the animal fluids. From the very complicated process, however, employed to obtain it, and from all he has stated with regard to it, some doubts may remain on the subject, at least with regard to this last opinion.

Besides the sugar of milk, which is the principal ingredient dissolved in the serum, there are present some other saline substances, which remain dissolved in the liquor after its crystallization. These, according to Scheele and Vauquelin, are principally muriates of lime, potash, and soda, with phosphates of lime, magnesia, and iron. According to Berzelius, scarcely any other alkali than potash is to be found in milk. Schwarz has given as the saline ingredients and their proportions in cows milk, in 1000 parts, phosphate of lime 1.805, phosphate of magnesia 0.170, phosphate of iron 0.032, phosphate of soda 0.225, muriate of potash 1.350, lactate of soda 0.115: human milk contained rather a larger quantity of the phosphates *. According to Thenard and Lagrange, there is always a little

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* Annals of Philosophy, vol. v. p. 41.

free acetic acid in fresh milk, which may be obtained from it by distillation.

Such is the composition of milk. It consists of an oily substance, of the caseous matter, of the sugar of milk, and of a small portion of neutral salts, and a little free acetic acid dissolved in water. The union of the three first, two of which approximate to the nature of vegetable, and the third to that of animal matter, renders it a fluid at once nutritive and easy of digestion; and, as Vauquelin has remarked, the presence of phosphoric acid with lime and iron, fit it for the formation of blood. Berzelius gives the following as the composition of milk, exclusive of the cream,—water 928.75, cheese with a trace of butter 28, sugar of milk 35, muriate of potash 1.7, phosphate of potash 0.25, lactic acid, acetate of potash with a trace of lactate of iron 6, earthy phosphates 0.3. Cream of the specific gravity 1.0244, was composed of butter 4.5, cheese 3.5, whey 92. The proportion of sugar of milk is undoubtedly stated too large, and the quantity of butter in cream too small.

SECT. IV.—OF LYMPH. OF MUCUS.

THE fluid contained in the lymphatic vessels, and passing into them either from the extremities of the arterial branches, or by absorption from the surface of the internal parts of the body, has from its origin been regarded as analogous to the serum of blood. This, however, is not established; and it is probable, that though derived from that fluid, it may have undergone some alteration; its properties therefore require to be noticed. They are but imperfectly known, from the difficulty of procuring it in a pure state.

Lymph is pellucid and insipid: it is said to be slightly viscid, miscible with cold water, and coagulated by heat, by the acids, and by alkohol. If these properties belong to it, it might be regarded as a solution of albumen; but there is some uncertainty whether the observations refer to pure lymph or to the serum of the blood, from these fluids having been assumed to be the same. Mr Brande collected the transparent colourless fluid found in the thoracic duct of animals that had been kept without food for 24 hours, and as it seemed to differ in no respect from that contained in the lymphatic vessels, he considered it as lymph. It was miscible with water in every proportion; did not affect the vegetable colours; was not coagulated by heat, nor by acids, or alkohol, but was rendered slightly turbid by the last re-agent: evaporated to dryness it gave a very small residuum, which slightly changed the colour of violet to a green, and by incineration gave a minute portion of muriate of soda.

Lymph undergoes, on the surfaces on which it is effused, a degree of inspissation, probably from its watery part being absorbed; it then forms what has been named Mucus, which covers the passages and internal membranes of the body. This term is however rather vague. Mr Hatchet had regarded it as similar to gelatin, only that when heated it does not become gelatinous. Dr Bostock applied it to denote a peculiar principle, existing in what is usually named Mucus, as well as in the serum of the blood, and in a number of the animal fluids. It may be obtained solid by evaporation, and is again soluble in water. It is insoluble in alkohol or ether. It neither coagulates, nor becomes gelatinous, when its solution is heated; characters by which it is distinguished from albumen and gelatin. Neither is it precipitated by tannin, or by corrosive muriate of mercury. The acetate of lead, or Goulard's extract, produces a copious white precipitate with it, and this forms its most certain test. Dr Bostock has remarked its resemblance in these properties to vegetable gum [*]. Fourcroy gave a still more extensive signification to the term, considering it as a principle contained in almost all the fluids, and in many of the solids of the body.

There is, however, no conclusive evidence for the existence of any well defined principle of this kind. Berzelius, while denying its existence, has supposed that the principle so named is lactate of soda, with an adhering portion of animal matter, an opinion almost equally vague. It has already been remarked, under the history of the blood, that the principle named Mucus, supposed to exist in the serum, is probably a small portion of residual albumen, modified by dilution, and the intermixture of saline matter: and the liquid mucus covering the surfaces of the membranes, and discharged from some of them in considerable quantity, seems to be inspissated serum or lymph.

The mucus of the nostrils affords a form of it, under which, from its quantity, it is easily examined. It was made the subject of investigation by Fourcroy and Vauquelin. As first secreted, it is liquid and clear, a little viscid, without smell, and of a taste somewhat saline; it soon becomes viscid and glairy from the action of the air, and in this state is not very miscible with water, nor does it dissolve. Boiled with water it shews no sign of coagulation. Evaporated by a gentle heat, it affords crystals of muriate and carbonate of soda, and phosphates of soda and lime. From the carbonate of soda it contains, it renders green, paper stained with the juice of the mallow. It also contains an animal matter not albuminous, but which becomes thick from the action of the oxygen of the atmosphere, or of oxymuriatic acid, and acquires opacity and a yellowish or greenish colour. The acids added in small quantity thicken it, but in a larger proportion they re-dissolve it, giving it different colours. The alkalis at first thicken, and then dissolve it. The alkaline or earthy salts do not dissolve it. It is little liable to putrefaction, when kept even in a humid state *. According to Berzelius, it contains mucous matter and albumen, with soda, lactate of soda, and muriate of potash and soda. The mucus of the Trachea is similar.

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[*] Nicholson's Journal, vol. xi. p. 251. vol. xiv. p. 144.

Fourcroy and Vauquelin observed, that the liquid which forms the tears is nearly the same with the nasal mucus. It is clear as water, without smell, having a taste somewhat saline; it renders green, paper tinged with juice of violet or mallow, a property which appears to be owing to the presence of soda. When heated it is inspissated; from exposure to the air, it becomes also viscid, and acquires a yellowish or greenish colour. It affords cubic crystals, containing an excess of alkali which alkohol dissolves, leaving the mucous part undissolved. In this inspissated state it is insoluble in water. The alkaline solutions which have no effect on the liquid, as it is first secreted, dissolve it after it has suffered this change, and restore to it its fluidity and transparency. The acids exert no action on it at its first discharge, except saturating the free soda. When it has been inspissated by exposure to the air, sulphuric acid disengages carbonic and muriatic acid gases, by decomposing the muriate and carbonate of soda which it contains: oxymuriatic acid causes coagulation. Alkohol forms white flocculi in this liquid. From these results, it follows, that the tears are formed of a large quantity of water, which holds in solution animal matter, with various saline substances,—muriate of soda, pure soda, phosphate of soda, and phosphate of lime. The last, when it accumulates, forms the concretions sometimes found in the lachrymal glands †.

A peculiar modification of Lymph seems to form Pus.

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* Fourcroy's System, vol. ix. p. 452.

† Ibid. vol. ix. p. 426.

In phlegmonic inflammation, the vessels exert a certain action, whence an increased portion of fluid is poured out, and this is changed in its properties from that which constitutes the usual discharge from the exhalents. From ulcerated surfaces, or abscesses, a similar fluid, still farther changed perhaps in its properties, is effused. These constitute the different varieties of Pus, or Purulent matter. The distinction between these and the Mucus of the membranes in some of its states is extremely slight. Their external appearance is similar, and though numerous experiments have been made to establish discriminating characters between them from chemical properties, from the supposed importance of determining by this means the nature of the expectorated fluids in some diseases of the lungs, the success of these has been only imperfect. Perhaps, indeed, no essential distinction exists between the different varieties passing insensibly into each other, according to the action of the vessels from which they have been discharged. The discriminating characters between Mucus in some of its intermediate states, and Pus from ulceration, are founded principally on the action of acids, mucus being dissolved more readily and more perfectly than pus, and the solutions of the former being more permanent, while those of the latter are decomposed and rendered turbid by the affusion of water. Some of these distinctions were pointed out by the younger Darwin *. And an ample investigation of these fluids in their principal varieties, was given by Dr Pearson †. Their general composition he inferred to be albumen, with saline matter, chiefly muriate of soda, potash, phosphate of ammonia and of lime, carbonate of lime, a sulphate and a minute portion of oxide of iron. And the chief differences between them seemed to be in the proportions of these ingredients, and more particularly of the

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* Experiments on Pus and Mucus.

† Philosophical Transactions, 1809, 1810.

albuminous matter to water. The thickest contained the largest quantity, and the smallest proportion of the saline substances.

SECT. V.—OF SALIVA. OF THE PANCREATIC FLUID.

THE fluid secreted in the salivary glands is designed to promote the mastication, and perhaps the digestion of the food. Its taste is slightly saline; it has a slight degree of viscidity; hence it is frothy, or retains the air entangled in it, which is probably owing to the mucus of the membrane mixed with it, and this mucus, according to Berzelius, subsides slowly after dilution. It does not mix readily with water: by trituration it may be diffused through it; but a portion remains undissolved, probably this mucous matter. When exposed to the air, a pellicle forms on it; it becomes turbid and deposites flocculi, changes which have been ascribed to oxygenation: it has been said, indeed, to have an unusual tendency to absorb oxygen; and hence it has been affirmed, that it promotes the oxidation of the metals; the extinction of mercury by trituration being facilitated by it, and even gold and silver leaf being oxidated when triturated with it *.

When the liquid formed by triturating saliva with water is heated, it is slightly coagulated. This denotes the presence of albumen. It is also coagulated or inspissated by alkohol, and by the stronger acids. The fixed alkalis and the earths cause an ammoniacal odour to exhale from it, by decomposing the ammoniacal salts it contains: the alkalis at the same time dissolve it. Lime-water throws down a precipitate of phosphate of lime; and oxalic acid detects the presence of lime in small quantity. The me-

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* Fourcroy's System, vol. ix. p. 445.

tallic solutions, especially the nitrates of lead, mercury, and silver, cause an abundant precipitation; partly from their action on the animal matter, and partly by decomposing the phosphates and muriates it contains. Acetate of lead, or Goulard's extract, produces a copious precipitate in saliva diluted with water and rendered clear by filtration *.

According to Berzelius, the peculiar animal matter of saliva is obtained by evaporating to dryness, adding alkohol which dissolves its saline ingredients, with the exception of a little free soda, which may be removed by alkohol acidulated with acetic acid. The residue is mucus, mixed with the peculiar matter; and this last may be dissolved by water. By evaporation it leaves a transparent mass, soluble again in water. Its solution is not precipitated either by alkalis or acids, or sub-acetate of lead, muriate of mercury, or tannin, nor does it become turbid by boiling. The saline ingredients are alkaline muriates, lactate of soda, and pure soda. The composition of the entire saliva, according to the same chemist, are water 992.9, peculiar animal matter 2.9, mucus 1.4, alkaline muriates 1.7, lactate of soda and animal matter 0.9, pure soda 0.9 †.

The concretions which are sometimes deposited in the excretory ducts of the salivary glands, are stated by Fourcroy to consist of phosphate of lime with mucus; and the incrustation formed on the teeth from the saliva, and known by the name of Tartar of the teeth, is said to be of a similar nature. This last substance is stated by Berzelius to be composed of 79 of earthy phosphates, 12.5 of mucus, and 8.5 of other animal matter.

The similarity of the Pancreatic Juice, or liquid secreted by the pancreas, to the saliva, has always been ob-

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* Bostock, Nicholson's Journal, vol. xiv. p. 147.

† Medico-Chirurgical Transactions, vol. iii.

served by physiologists, but it has undergone little chemical examination. Dr Fordyce, from a small quantity which he procured of it, found it to be liquid and colourless, having a taste slightly saline. On allowing it to evaporate, crystals were deposited, similar to those from saliva, and muriatic acid was indicated by the test of nitrate of silver. On evaporation also a colourless mucus was obtained, which re-dissolved in water, though the compound with water, to use Dr Fordyce's expression, is not very diffusible through water *. From these facts it appears to be analogous to saliva, and probably, as physiologists have conjectured, serves the same purpose in promoting the digestion of the food.

SECT. VI.—OF THE GASTRIC FLUID.

No fluid presents more singular properties, than that which is secreted by the glands of the stomach, and which is of so much importance in the process of digestion. From its connection with that process, its properties have been often the subject of investigation, and a number of facts with regard to it have been discovered by the labours of Reaumur, Stevens, and Spallanzani.

The principal difficulty in submitting it to experiment is that of obtaining it pure; for as there is no duct whence it can be collected, it is always liable to be mixed with the contents of the stomach. The method which Spallanzani employed, was to cause an animal to swallow small pieces of sponge, when it had fasted so long as that the food might be supposed to have been evacuated from the stomach, and after some hours withdrawing them by a string attached to them. By pressing them over a glass capsule, the gastric

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* Treatise on Digestion, p. 70.

fluid which they had imbibed was obtained. It has also been collected from the stomach of an animal newly killed, which had previously been kept some hours without food; but the quantity that can be thus procured is not considerable. In the operation of vomiting it frequently happens, that after the mixed contents of the stomach had been discharged, a colourless fluid, more or less viscid, is brought up, which has been regarded as the gastric juice. Dr Fordyce has remarked, however, that he had often examined this, and found it to be water, with a small quantity of saline matter, and to be destitute of one of the most characteristic properties of the gastric fluid, that of coagulating milk.

The gastric fluid obtained by Spallanzani, was, in all the orders of animals from whom he procured it, whether gramenivorous or carnivorous, similar in appearance and physical qualities. If unmixed with any of the food, it was clear, or its transparency was at least little inferior to that of water. Its taste was always somewhat saline, frequently also bitter: this bitterness, as well as a tinge of yellow which it sometimes had, being owing, as he supposes, to the presence of bile. He could not discover in it any indication of acidity, except sometimes in animals feeding on vegetables, and the acidity was then evidently owing to the intermixture of the food, and the changes it had undergone *: it was equally free from any alkali: when triturated with lime, it was found to emit a fœtid odour. It precipitated silver in the state of muriate, from nitrate of silver: evaporated it gave a solid residuum, deliquescent, and having an unpleasant odour. Subjected to destructive distillation, muriate of ammonia was sublimed †.

To this very imperfect account of the qualities of the gastric fluid, some facts were added by Macquart and Vau-

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* Spallanzani's Dissertations, vol. i. p. 527.

† Ibid. p. 55. 87. 282. 529.

quelin. They obtained it from the stomachs of sheep and calves; they always found in it free phosphoric acid and phosphates. A small quantity of albumen was separated from it by the action of acids, besides a portion of mucus or gelatinous matter *.

Spallanzani had observed, that the gastric fluid is little liable to putrefaction. Obtained from his own stomach by vomiting, he remarks, that "it did not change colour or taste, nor did it acquire any bad smell, though kept above a month, in the hottest season of the year;" and he observes, that this is a property common to every gastric fluid he had examined †. Nay, he found, that it prevents substances from putrefying, and even that animal matter, which had become offensive, was rendered free from this, by maceration in the gastric fluid, either out of the body or in the stomach of the animal ‡. These properties were not observed by Macquart and Vauquelin in the gastric fluids they examined; on the contrary, they became corrupted in a few days. The observation of Spallanzani was, however, confirmed by the experiments of Stevens.

The most singular property of this fluid, and one which is undoubtedly chemical, is its solvent power with regard to the food,—a power established by the multiplied researches of Reaumur, Stevens, and Spallanzani. Reaumur inclosed articles of diet in metallic tubes open at both ends, which he forced animals to swallow; employing those substances with regard to each on which they naturally feed. By this contrivance he avoided the action of pressure and trituration, which had been considered as principal causes of digestion, and exposed the food merely to the action of the gastric fluid. He found, that in animals

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* Fourcroy's System, vol. x. p. 11.

† Dissertations, vol. i. p. 185. 285.

‡ Ibid. p. 348. &c.

with a membranous stomach, and which usually feed on flesh, the inclosed food was dissolved, more or less completely, according to the time during which the tubes were allowed to remain in the stomach; and he hence inferred, that the gastric fluid of these animals is possessed of a solvent power. But in those animals which have a muscular stomach, capable of strong contraction, and therefore of performing the office of trituration, the substances inclosed (grains chiefly on which these animals feed, though sometimes also grass, or even flesh) were not dissolved; and hence he concluded, that in these animals the gastric fluid is not a solvent, and that the digestion of the food is effected by trituràtion. Spallanzani rectified this conclusion; he shewed, that the trituration is necessary only to bruise the food, and thus prepare it for the action of the gastric fluid, and that when previously bruised, or when from any other preparation it is in a soft or humid state, and inclosed in tubes, it is dissolved by these being allowed to remain in the stomach [*]. He further found with Reaumur, that in animals with a membranous stomach, the solution of the food inclosed in tubes takes place very readily [†]. And what is still more decisive with regard to the solvent power of the gastric fluid, he found, that the different substances used as food, both flesh, bread, grain, and grass, submitted to its action out of the body, at a temperature not higher than that of animals, were dissolved [‡]. It appears from his researches, that in animals with a membranous stomach, the solvent power is greater than in those with a muscular stomach; and in some of the former, in the dog for example, or the eagle, the solvent power is very considerable, the hardest bone inclosed in tubes being speedily dissolved.

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[*] Dissertations, vol. i. p. 55.

[†] Ibid. vol. i. p. 69. 70. 108. 258.

[‡] Ibid. p. 93. 170.

With the experiments of Spallanzani, those of Stevens in general agree *. Availing himself of the opportunity of making experiments on a man who had the power of swallowing hard substances without injury, he gave to him almost all the articles of food, vegetable or animal, inclosed separately in hollow spheres of silver, perforated with holes, and found that they were speedily dissolved. And continuing his experiments on animals, he established nearly the same results as Spallanzani had done. He found too, that the gastric juice out of the body exerts its solvent power. Half an ounce of the gastric juice of a dog was put into a phial with twelve grains of roasted beef, and the same quantity of the same beef was put into another phial with water. Both were exposed to a temperature of 102 or 104: in eight hours, the beef in the gastric fluid was dissolved, while that in the water was not sensibly altered: in twenty-four hours, the latter was putrid, while the former had merely a pungent odour, probably from a slight scorching from the heat. When the experiment was repeated with flesh masticated, the solution was sooner completed; and in a similar manner, other substances, both animal and vegetable, were dissolved.

In one point, the experiments of these physiologists do not perfectly correspond. Stevens found, that those kinds of food on which animals do not naturally feed are not dissolved when introduced in these balls into the stomach; that if tubes or balls, for example, containing flesh, fish, grass, and herbs, be introduced into the stomach of a sheep, the latter are dissolved, while the former are not altered. The experiment was repeated on the ox with a similar result; and hence it appears, that in those animals which usually feed on vegetables, animal food is not dissolved by the gastric fluid. Spallanzani, however, obtained a result somewhat different; in animals which feed principally on

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* Dissertatio Inauguralis, Edin. 1777.

grain, as ducks, hens, and turkeys, flesh introduced in tubes into the stomach being dissolved [*]; while in those which feed usually on flesh, as the crow, farinaceous grains, previously bruised and introduced in tubes, were likewise dissolved [†]. These animals, however, do not seem naturally much limited to one kind of food, but can subsist on very different substances. And it is admitted by Spallanzani, that some species, as birds of prey, are incapable of digesting vegetables [‡]. It therefore rather appears, that the solvent power of the gastric fluid is in a great measure limited to the kind of food on which the animal naturally subsists, though the stomach is undoubtedly capable of so far adapting itself to the food received, that the animal can at length be brought to be nourished by substances the most opposite to those on which it naturally feeds. In those animals which feed both on vegetable and animal matter, as in man, both are dissolved by the gastric fluid.

The solvent power of this fluid is well shewn by its action on the stomach itself; it frequently happening that an erosion, or a solution of the depending part of the stomach, is discoverable after death, as Mr Hunter first pointed out [||]. And no fact better shews, how far the presence of vitality suspends or counteracts the usual chemical powers, since, during life, the stomach does not suffer from the action of this fluid. Stevens has, however, stated some facts to prove, that this is to be understood with some limitation, and that animals, even while alive, are in some cases subject to the process of digestion [§].

These facts with regard to the solvent power of the gastric fluid are truly singular; they are such as could not be inferred from any quality it is known to possess, or from any other chemical agency it appears to be capable of exerting: they admit, therefore, of no explanation, and, in our present imperfect knowledge of its nature, must be received merely as ultimate facts. The chyle of animals who live entirely on vegetable food, of the horse for example, contains principles strictly analogous to those of animal matter. The rapid change, therefore, says Vauquelin, which vegetable substances suffer in the organs of digestion of animals, and their total conversion into animal matter, are truly astonishing; a few hours being sufficient to cause the characters and nature of vegetable matter to disappear entirely. The powers, therefore, exerted in digestion must be highly energetic.

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[*] Dissertations, vol. i. p. 56.

[†] Ibid. p. 65.

[‡] Ibid. p. 217. 288.

[||] Philosophical Transactions, vol. lxii. p. 447.

[§] Dissertatio Inauguralis, p. 58.

SECT. VII.—OF BILE. OF BILIARY CALCULI.

BILE is a fluid secreted by the liver from the venous blood which has circulated through the abdominal viscera; it enters the intestines, and appears designed to serve some important purpose, from the large quantity of it secreted. It has generally been considered as an assisting agent in the process of digestion, or at least in the formation of chyle; and, in support of the latter conclusion, the fact has been stated, that no traces of the chyle are to be discovered previous to the intermixture of the bile with the digested food. It is no argument against this opinion, that the bile cannot be discovered by any of its properties in the chyle; for these may be changed by the combination, or some of its principles only may enter into the composition of that fluid, while others are discharged as excrementitious. The singularity deserves to be remarked, that it is formed from venous blood, while the other secretions appear to take their origin from arterial blood. This deviation would lead to the conjecture, that a large proportion of carbon and hydrogen is necessary to its constitution; it will accordingly appear from its analysis, that its principal ingredient is highly inflammable, and is similar in its properties to the vegetable resins, in the composition of which carbon and hydrogen predominate; and the hypothesis which has been proposed is not improbable, that that portion of it which is excrementitious is designed to convey an excess of hydrogen from the system. Its secretion, under this point of view, may be regarded as subordinate to respiration, and as freeing the blood from principles which could not, without inconvenience, be entirely abstracted by the action of the air.

The bile, when first secreted, is liquid and thin; in this state, a portion of it constantly flows into the upper part of the intestinal canal. But in many animals, there is a particular reservoir, the gall-bladder, into which a quantity is received, which from absorption becomes more thick, and which occasionally flows into the intestines. The qualities of the bile do not seem to be otherwise much altered in this organ, and its inferior importance is demonstrated by the fact, that in many even of the more perfect animals it is wanting. It is this cystic bile, however, as it is named, or bile collected in the gall-bladder, that has been generally examined, as it is that which is most easily procured.

It has always a certain degree of tenacity, more or less, according to the time during which it has been retained in the gall-bladder, and probably according to the energy of absorption. It feels unctuous, or rather soapy: its specific gravity is 1.026: its colour is yellowish green, and, in some animals, nearly pure yellow: its odour is faint, and peculiar: its taste is extremely bitter, this bitterness being strong even in its most dilute state, and becoming intense when the bile, from stagnation, is thick and viscid.

Bile, from its obvious importance in the living system, has often been submitted to chemical examination. For the principal facts with regard to it, we are indebted to Cadet *, Ramsay †, and more lately to the investigations of Thenard ‡.

Bile at a moderately warm temperature, suffers spontaneous decomposition, emits a fœtid odour, and seems to pass into putrefaction.

When exposed to a gentle heat, a large quantity of watery liquid, about 90 parts from 100, passes over; this has the odour of the bile, but not its taste. The residual matter is thick and tenacious, of a dark brown colour, intensely bitter, deliquescent, and soluble in water; after some time, it acquires a peculiar smell similar to that of ambergrise or musk: bile itself acquires this smell on being kept, and communicates it to the water distilled from it. When the extract of bile, as the substance which is obtained by evaporation of the watery part is named, is exposed to a heat gradually raised, it is decomposed; water containing sulphuretted hydrogen, distils over; a liquid next passes, brown and very fœtid, containing carbonate and acetate of ammonia; this is succeeded by empyreumatic oil; more carbonate of ammonia sublimes, and carbonic acid, carburetted and sulphuretted hydrogen gases, are disengaged. A spongy charcoal remains, which burns easily, and which, when exposed to the air, affords an efflorescence of carbonate of soda. By incineration, there are obtained from it carbonate of soda, amounting to nearly half its weight, with a little muriate of soda, and some traces of iron ‖, and, according to Fourcroy, phosphate of soda and phosphate of lime. The dry matter obtained by the evaporation in this experiment, takes fire if heated under free ex-

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* Mémoires de l'Acad. des Sciences, 1767.

† Dissertatio Inauguralis, Edin. 1757.

‡ Mémoires de la Sociéte d'Arcueil, tom i. p. 23. 46.

‖ Cadet, Mémoires de l'Acad. des Sciences, 1767, p. 351.

posure to the air, and yields the same salts after the combustion, and, according to Thenard, a small portion of sulphate of soda.

Bile mixes with water in every proportion, and even in its inspissated state is readily dissolved by it. The solution changes the colour of violet, or mallow, to a green, indicating the presence of a free alkali.

The acids decompose bile. If a few drops of acid be added, little precipitation is occasioned, but a liquor of a reddish tint is obtained. If more be added, a copious precipitate is formed, of a greenish colour, especially when thrown down by muriatic acid; after some hours, as Cadet observed, much of this coagulum disappears, and there remains on the filtre a substance similar in its properties to albumen. The liquor obtained by filtration, has an extremely bitter taste; when evaporated, it deposites flakes, tenacious and inflammable, melting and burning when kindled, with much smoke like a resin, and soluble in alkohol. The liquor poured off from this contains soda, as it affords, by evaporation, the salts formed by the union of soda with the acid that has been employed in the experiment *. These are the general effects which are somewhat diversified by the different acids. Concentrated sulphuric acid separates dense flocculi, and gives a deep colour; diluted sulphuric acid renders bile intensely green. Muriatic acid also precipitates it of a green colour, which from heat assumes a violet tinge. Nitric acid precipitates it green in the cold, but, when heated, assumes a red, and ultimately a grey colour; by evaporation it assumes a golden yellow colour, and the bile is converted partly into oxalic and prussic acids. Oxymuriatic acid whitens it and renders it turbid, by coagulating its albumen, and at the same time converts its resin into a white fatty substance †.

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* Cadet, Mémoires de l'Acad. des Sciences, 1767, p. 540.

† Fourcroy, ibid. 1789, p. 515.

The action of alkohol on bile affords results which point out most clearly the nature of its immediate principles. When the alkohol is poured upon it, a coagulum is formed, which floats in a liquid of a green colour. When this is separated by filtration, there remains on the filtre a white viscid substance, having scarcely any bitter taste, and very putrescible, approaching therefore in its properties to albumen, and which has hence received the name of the Albumen of Bile. It can likewise be separated, though imperfectly, by heat, bile becoming thick when its temperature is raised to 170°, independent of any evaporation; it is this matter too, which forms the basis of the coagulum separated by acids; it is insoluble by itself in water, but it combines with soda, and is rendered soluble.

The filtered liquor obtained in the coagulation of bile by alkohol, retains the green colour and the bitter taste of the bile. When evaporated, it affords a concrete substance of the same colour, inflammable, fusible at 120°, soluble in alkohol, and precipitated by the affusion of water. It is also soluble in the alkalis, from which it is precipitated by acids. From these properties, in which it approaches to the vegetable resins, it has been named the Resin of the Bile, and it appears to be the principle in which the colour, odour, and taste reside.

Besides these principles, Cadet observed in the bile a kind of saccharine matter, which approaches in its properties to sugar of milk. Verheyen had alluded to the saccharine taste found in the bile when it has been thickened by evaporation, and again dissolved in water; but the principle on which this depends had not been discovered prior to Cadet's researches. He recognised it in different experiments. Thus, when bile was decomposed by muriatic acid, and the muriate of soda obtained by evaporation of the residual liquor, he found among the crystals of this salt, another matter in trapezoidal crystals, in which he observed the resemblance in taste to sugar of milk. And he also procured it by decomposing bile by nitric acid; it remains in the residual liquor when the coagulum has been separated, united with a portion of oily or resinous matter; on saturating this liquor with an alkali, this saccharine matter is precipitated, the alkali attracting the acid and the oily matter. It has been more lately examined by Thenard. To separate it, he added to bile sub-acetate of lead, that is, acetate of lead boiled with an excess of litharge; the albumen and resinous matter were precipitated in combination with oxide of lead; the liquor being filtered, the excess of lead remaining in it was separated by sulphuretted hydrogen; and by evaporation of the liquid after this operation, a substance was obtained, the taste of which was saccharine and acrid. This matter he named Picromel. He found it to be soluble in water and in alkohol; it is not crystallizable; it does not ferment with yeast; it precipitates the solutions of nitrate of mercury, and those of iron, and of sub-acetate of lead; is not affected by infusion of galls; and it forms, with soda and resin of the bile, a compound not decomposed by acids, alkalis, or earths.

Its most important property is that of dissolving the resinous matter of the bile. This had been supposed to be dissolved by the alkali which experiments proved the bile to contain. But Thenard found that the quantity of alkali is not sufficient for this purpose; it is aided by the solvent power of the picromel,—the resinous matter, picromel, and soda, forming a ternary soluble combination, which, with a little albumen and certain salts, constitute bile.

The saline substances which the bile contains, are, besides the soda, the existence of which has been already stated, muriate, sulphate, and phosphate of soda, phosphate of lime, and oxide of iron. Thenard gives the following as the proportions, water 700 parts, solid matter 100 parts, consisting of resin 24, saccharine substance or picromel 60, yellow albuminous matter 4, soda 4, phosphate of soda 2, muriate of soda 3.2, sulphate of soda 0.8, phosphate of lime 1.2, oxide of iron a minute trace.

Little was known with regard to the varieties of the bile in different animals. Thenard instituted some inquiries on this subject. His first experiments were made on ox bile; that of the sheep, dog, and cat, he found to be similar to it; that of the hog does not contain either albuminous matter, or picromel, but resin in large quantity, with soda, and some saline substances. The bile of birds, though it has a great analogy with that of quadrupeds, differs from it in containing a large quantity of albuminous matter, and in the picromel obtained from it being not sensibly saccharine, but extremely bitter and acrid; there are also only minute traces of soda; and acetate of lead does not precipitate its resinous matter. The bile of fishes is usually less bitter than that of quadrupeds. Thenard found, that that of the thornback and the salmon is of a yellowish white colour; it affords by evaporation a matter very sweet, and slightly acrid, and it appears to contain no resin: that of the carp and the eel is very green, extremely bitter, contains little albuminous matter, and affords soda, resin, and a matter sweet and acrid, similar to that from the bile of the salmon. Human bile is described by Thenard as varying in colour, being sometimes green, more frequently of a brownish yellow, sometimes colourless; its taste is very bitter; it is rarely perfectly limpid, but contains a quantity of yellow matter in suspension. It becomes turbid on boiling, and by evaporation affords a brown mass equal to an eleventh part of the bile evaporated, which when calcined afforded the same saline substances as ox bile. The acids decompose it, and throw down an abundant precipitate of albumen and of resin. Acetate of lead changes it into a liquor slightly yellow, in which no picromel is found, and which contains only acetate of soda, and some traces of animal matter. He gives the following as the composition of human bile, 1000 of water, with 100 of solid matter, consisting of from 2 to 10 of a yellow matter insoluble, which is suspended in the bile, 42 of albumen, 41 of resin, 5.6 of soda, and 4.5 of phosphates of soda and lime, sulphate and muriate of soda, and oxide of iron. He adds, that when the liver is enlarged, the bile which it secretes appeared to be less resinous; and when the disease is much advanced, it is principally albuminous, without much bitterness *.

Berzelius has given altogether a different view of the preceding results, and of the composition of the bile. According to him, there is no such principle as the resin of the bile, nor does it contain albumen: what has been considered as albumen, is mucus. But its chief constituent which gives it colour and taste, is a peculiar matter, which is of itself soluble in water, and does not owe this solubility, as has been supposed, to any free alkali; since, when this is neutralized by an acid, it is not, according to his statement, separated. It also dissolves in alkohol in all proportions. Like albumen and other animal principles, it combines with acids in two proportions, forming compounds of different degrees of solubility. Acetic acid, which forms soluble compounds with albumen, does the same with the peculiar matter of the bile; and hence this matter is not precipitated on adding this acid to bile, but it falls down from the action of sulphuric, nitric, or muriatic acid. It is this sparingly soluble compound of the principle of bile with a mineral acid, which has been mistaken for a resin, as it possesses the external characters of a resin, is fused when heated, dissolves in alkohol, and is precipitated in part at least on the addition of water. The alkalis, alkaline earths, and acetates, decompose and dissolve it, the former by de-

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* Mémoires de la Société d'Arcueil, tom. i. p. 54.

priving it of part of its combined acid, the latter by yielding acetic acid, which renders it soluble in water. This peculiar biliary matter may be obtained pure, by mixing fresh bile with sulphuric acid diluted with three times its weight of water; a yellow precipitate first appears, which is to be removed, being chiefly mucus; fresh acid is then added as long as any precipitate is formed; the mixture is to be heated gently for some hours, and the green precipitate which is left is to be well washed with water. The sulphuric acid may be abstracted by digesting it with carbonate of barytes and water; the pure biliary matter remains in solution, communicating a green colour and all the peculiar properties of bile. When dried it resembles entire desiccated bile; it is soluble in alkohol, but not in ether, but is converted by ether into a kind of fatty substance. It yields no ammonia in distillation, and therefore contains no nitrogen. According to Berzelius, bile is composed of 80 of this biliary principle, 3 of mucus of the gall bladder, 9.6 of alkalis and salts, (common to all secreted fluids), and 907.4 of water *. The observations of preceding chemists must have been very incorrect if these views are just.

THERE are frequently formed in the gall-bladder concretions, derived, probably, from changes the bile suffers while it remains in that organ. These have been named Biliary Calculi, and have been repeatedly subjects of chemical investigation. They are not altógether uniform in their appearance, but vary in colour, texture, and hardness, and in their chemical characters.

The most common kind are of a lamellated structure,

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* Essay on Animal Fluids.

and consist of a substance resembling the animal fat named Spermaceti, disposed in crystalline laminæ. This peculiar matter appears first to have been taken notice of by Poulletier de la Salle: he found, that when these calculi are digested in alkohol, the liquid, on cooling, deposites brilliant crystalline flakes. Fourcroy, on examining it *, found, that it has a close resemblance in its properties to that species of animal fat which he distinguished by the name of Adipocire, and of which he considered spermaceti, as well as the fatty matter formed from animal substances under certain circumstances, as varieties. It melts, but requires a heat superior to boiling water: in fusion it has a smell like wax, and on cooling, forms a substance which breaks into crystalline laminæ. It is not soluble in alkohol in the cold; but when the alkohol is boiled on it, it is dissolved in a proportion, according to Fourcroy, of one part in nineteen,—according to Dr Bostock, one in thirty †. The solution, when it cools, deposites light brilliant scales. It is soluble in ether in the cold, and more abundantly if the ether be heated. Oil of turpentine dissolves in general biliary calculi; and according to Gren, it dissolves those which consist of this peculiar matter; yet Dr Bostock has remarked, that oil of turpentine acts on it with difficulty, and, even when digested with it at a boiling heat, dissolves it in a small degree only. Pure soda and potash dissolve it, and reduce it to a saponaceous state. Ammonia exerts little action on it, except when boiling. Nitric acid dissolves it, and, according to Fourcroy, converts it into a liquid similar to the oil of camphor, which becomes concrete. Chevreul has lately proposed to name it Cholesterine. He has remarked, in opposition to the statement of Fourcroy, that it does not form a soap with the

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* Mémoires de l'Acad. des Sciences, 1789, p. 725.

† Nicholson's Journal, 8vo, vol. iv. p. 137.

fixed alkalis, in which it differs from spermaceti. According to Pelletier, a new acid is produced by the action of nitric acid upon it, which he has named Cholesteric acid *.

This substance, Fourcroy has observed, is contained in greater or less quantity in nearly all the human biliary calculi, intermixed with other matter, but so far predominant as to form their basis. Hence they partake of its properties; are fusible, inflammable, and more or less soluble in the re-agents which dissolve it. Their texture is laminated or radiated: some are composed of it nearly pure; these consist of layers, soft and brilliant; in others, it is intermixed with a yellowish or greenish matter; and in some, this matter is in so large a proportion, that the other principle is disguised, and is discovered only by its deposition, when the calculus has been dissolved by hot alkohol; and often the calculus consists of layers, which, from their colour, appear to consist of these principles in different proportions.

Other calculi are sometimes found, particularly in the gall-bladder of quadrupeds, which have been supposed to consist chiefly of inspissated bile; but which appear to consist rather of this yellow substance. It must have undergone some other change than mere inspissation; for, as Dr Bostock has observed, it is nearly insoluble both in boiling water and in alkohol. Thenard has stated, that the biliary calculi in the ox are always homogeneous, and consist of successive layers of the yellow or albuminous matter of the bile.

To point out the distinctions among these calculi from mechanical structure, is foreign to their chemical history.

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* Annals of Philosophy, vol. xi. p. 468.

SECT. VIII.—OF URINE. OF UREE. OF URIC ACID. OF URINARY CALCULI.

THE fluid, secreted by the kidneys, is excrementitious, or is designed to convey from the body matter which, if retained, might prove injurious: acidification seems in particular to take place in this secretion, and hence it affords more saline substances than any other secretion, mixed, however, with other animal principles, which give appropriate characters. Some of these are even peculiar to urine; its chemical history is therefore of much importance, and has been the subject of many laborious researches. Margraaf began the scientific investigation of its composition. Some facts were discovered by Rouelle*. Scheele discovered the uric acid, and pointed out the existence of some other principles †. Cruickshank added a number of important facts on the modes of analysis, pointed out more clearly the principles existing in urine, both in a healthy and a morbid state, and distinguished the peculiar animal matter which it contains ‡. The nature of this principle, and its characters, were more amply developed by Fourcroy and Vauquelin, with some additional facts on the chemical history of urine ‖. And some results have been more recently added by Berzelius §, and others.

The colour of urine is pale yellow: its odour is peculiar, but not strong nor fœtid, such as it becomes when it has stood for some time: its consistence and specific gravity are rather greater than those of water: it is transparent, but deposites a light cloud as it cools, from the deposition of a little mucus from the bladder, and frequently becomes turbid from the separation of other ingredients. These qualities, however, are liable to variation, according to the length of time it has remained in the bladder after having been secreted, and according to the diet, quantity of drink, and other circumstances which influence the secretion.

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* Journal de Medicine, 1773.

† Chemical Essays.

‡ Rollo on Diabetes, 2d edit.

‖ Memoires de Instit. National, tom. ii. and iv.

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Urine, examined when immediately discharged, is in general sensibly acid, and reddens the infusion of litmus. But in a short time, from the spontaneous decomposition of its animal matter, a quantity of ammonia is evolved, which not only neutralizes the acidity, but renders the urine alkaline. Previous to this, however, it deposites, unless it has been in a very dilute state, part of the acid peculiar to it, Uric Acid as it is named, in minute crystals of a reddish colour, and in some states of the system this deposition is abundant, forming principally what is named the Lateritious Sediment. The deposition of this is soon interrupted, from the evolution of ammonia, which neutralizes it; urate of ammonia is then deposited; and, according to Berzelius, the red precipitate is super-urate of ammonia with mucus. Free phosphoric acid, if present, is likewise saturated, and the proportion of phosphate of ammonia thus increased; and the neutral phosphates of lime and of magnesia, which were retained in solution by the free acid, are deposited, the latter attracting a portion of ammonia, so as to form the triple phosphate of ammonia, and magnesia. As the decomposition proceeds, the ammoniacal odour becomes strong, and at length the urine is highly alkaline, from the presence of carbonate of ammonia, so as to change the vegetable colours to a green, and even to effervesce with acids. In this state it likewise, according to Fourcroy and Vauquelin, contains, neutralized by ammonia, a portion of acetic acid, derived, as well as the ammonia and carbonic acid, from the decomposition of the animal matter or urée. If kept until the whole of this is decomposed, there may be obtained from it, by evaporation, its remaining salts, which are principally phosphates and muriates, with bases of ammonia, soda, magnesia, and lime. In this spontaneous slow decomposition, oxygen is absorbed, according to Gay Lussac, from the air.

The acid contained in recent urine in a free state is principally the one denominated Lithic or Uric, and which, though in very variable quantity, is contained in all urine. Even when it is not spontaneously deposited, it may be detected by its tests, particularly by the pink colour which it gives with nitric acid; it is often made to precipitate, by concentrating the urine by evaporation, or it may be thrown down by the addition of an acid. This acid, however, scarcely reddens the vegetable colours, and as litmus is reddened by recent urine, it is evident that some other must be also present. It has been supposed to be the phosphoric, from the circumstance, that phosphate of lime is present, which requires an excess of this acid to retain it in solution. But, according to Thenard, it is the acetic, which may be obtained, by adding to the residuum of the evaporation of urine by a gentle heat, alkohol, and then adding to the spirituous solution thus formed, barytes, by which acetate of barytes is obtained *. According to Berzelius, it is the lactic, an acid which, as has already been remarked, he distinguishes from the acetic; and which may be procured, he states, by evaporating urine to the consistence of syrup, and adding alkohol; the substance remaining undissolved is acid, and by the addition of ammonia is decomposed, and the lactic acid combined with the ammonia becomes soluble in alkohol. By adding lime the ammonia is expelled, the lime may then be ab-

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* Nicholson's Journal, vol. xix. p. 69.

stracted by oxalic acid, and the lactic acid remains. A portion of benzoic acid was said by Scheele to be sometimes present in urine, especially that of children. Thenard has found, that it is also often wanting, even when the urine is acid; and Berzelius could never detect it. In the urine of horses and cows, it is sometimes contained in considerable quantity; in which case the other acids exist in smaller proportion, and the urée appears also to be deficient. Hence, by mere evaporation of the urine, and the application of a sufficient heat to the residual matter, the benzoic acid is sublimed; or it is precipitated when muriatic acid is dropped into the urine evaporated to the consistence of syrup. Proust had announced the presence of free carbonic acid in urine. Berzelius disputed this. But Vogel has confirmed it by a simple experiment,—placing urine under the receiver of an air-pump, with a vessel of lime-water, and exhausting the air, air-bubbles arose from the urine, and the lime-water became milky *.

When urine is exposed to a gentle heat, water, holding carbonate of ammonia in solution, is evaporated; the proportion of which increases as the evaporation proceeds. The liquid becomes turbid, darker in its colour, and stronger in its odour; and a flocculent matter, with a whitish powder, are precipitated: the former being supposed, by Fourcroy and Vauquelin, to be albumen, the latter being phosphate of lime and uric acid. When reduced to the consistence of thin syrup, on cooling, it passes to the state of a confusedly crystallized mass. If the liquor poured from this be evaporated, this is repeated; and in this way several successive formations of crystals, irregular, and of a brownish colour, take place, leaving at length a liquor deep coloured and of a thick consistence, in which the peculiar animal principle of urine exists in solution.

The saline matter obtained from urine by evaporation,

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* Annals of Philosophy, vol. vii. p. 56.

has long been a subject of chemical investigation; it was known to the alchemists, and engaged the attention successively of Margraaf, Pot, Rouelle, and Scheele. It had received the absurd name of Microcosmic Salt, and, from its fusibility, had also been named Fusible Salt of Urine. It was known to afford phosphorus by distillation. Margraaf recognised in it the presence of muriate of soda and phosphate of ammonia, and likewise phosphate of soda. Rouelle distinguished more clearly the phosphates of ammonia and soda, and described the methods of separating and purifying them. He announced also the presence of muriate of potash, which had been before confounded with the muriate of soda, and which, it now appears, is present even in larger quantity than the latter. He affirmed, that he had likewise extracted sulphate of soda; but this was supposed doubtful, and to have arisen from his having mistaken phosphate of soda for it. The sulphate of lime, which he also supposed he had discovered in this saline mass, was supposed, from the subsequent discovery of Scheele, to be phosphate of lime. But, according to Berzelius, urine does contain sulphuric acid, which may be detected by muriate of barytes, and which exists in the state of sulphate of soda, and sulphate of potash. Fourcroy and Vauquelin discovered phosphate of magnesia. Berzelius has detected in urine a small portion of fluate of lime, derived probably by absorption from the bones, in which he found this earthy salt to exist. These salts then, —the phosphate of soda, the phosphate of ammonia, phosphate of magnesia, phosphate of lime, muriate of soda, muriate of potash, muriate of ammonia, and the triple compounds of phosphate of soda and ammonia, and phosphate of magnesia and ammonia, and the sulphates, with a portion of uric acid more or less saturated with ammonia, and urée, compose the crystallized mass obtained by the evaporation of urine. They exert mutual affinities, in consequence of which their perfect separation is difficult, and even their respective properties are modified: the muriate of soda, for example, in crystallizing, takes the form of an octaedron, and not, as when pure, that of a cube; and the muriate of ammonia, instead of appearing under its usual form of a prism, crystallizes in cubes. These modifications, according to Fourcroy and Vauquelin, are owing principally to the action of the urée. It is also to be observed, that all these salts do not pre-exist in the urine; those containing ammonia derive this alkali partly from its formation during the evaporation: and as the combinations must be modified by the concentration, it is not easy among so many substances to determine what really are the original ingredients. The muriatic, phosphoric, and fluoric acids, appear to pre-exist in the blood, and also perhaps the acetic or lactic. The sulphuric, uric, and benzoic, seem to be formed in the kidneys.

It is difficult to determine the proportions of these products to each other, as they are liable to variation from the circumstances influencing the secretion. Mr Cruickshank, in his analysis of urine, undertaken in the course of Dr Rollo's investigation of the nature of diabetes, first gave precise information on this point *. "By evaporation 36 oz. yield a residuum, varying from one ounce to one and a half; this consists of muriates of potash and soda, phosphates of soda, lime, and ammonia, phosphoric and lithic acids, with animal extractive matter. Their relative proportions in a healthy state may be nearly as follow:

	oz.	dr.	gr.
Muriatic salts,	0	1	0
Phosphoric salts,	0	3	50
Lithic acid and phosphate of lime, with excess of acid,	0	0	25
Animal extractive matter, (urée),	0	3	40

Of the muriatic salts, the muriate of potash is in gene-

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* Rollo on Diabetes, 2d edit.

ral the most prevalent, and is distinguished from the muriate of soda by crystallizing by cooling, and affording super-tartrate of potash on the addition of tartaric acid. When the phosphate of ammonia is abundant, the saline mass is in general very fusible. The phosphate of lime and lithic acid are generally deposited as the urine cools. These substances may be easily distinguished, by dissolving them in twice their weight of nitrous acid, diluted with a little water, and evaporating to dryness: the dry mass, when hot, will assume a beautiful deep rose or crimson colour, when the lithic acid is present, but will continue white if heated even to redness, or have only a slightly greenish tinge when there is nothing but phosphate of lime. Their relative proportions may be ascertained by exposing the mixed mass for some time to a red heat in a crucible; in which case, the lithic acid will either burn out or evaporate, leaving the phosphate in a pure state.

"The quantity of extractive matter is more variable than that of any other substance; hysterical, or crude urine (as it has been called), containing hardly any, while that of concoction abounds with it."

If the entire mass of urine be evaporated, and the solid matter be urged by a strong heat, it affords very fœtid carbonate of ammonia, in large quantity, with a little prussiate of ammonia, an empyreumatic oil, gases composed principally of carbon and hydrogen: muriate of ammonia is also sublimed; and towards the end of the process, if the heat be raised high, a small quantity of phosphorus distils over, produced by the decomposition of the phosphoric acid in the phosphate of ammonia. It was by this method that phosphorus was procured by Kunckel and Boyle. The coal remaining at the end of the process contains the salts which have not been decomposed,—muriate of soda, and phosphates of soda and lime.

One peculiar ingredient has been stated to exist in urine by Berzelius, which does not appear to be combined with any base,—siliceous earth. It is obtained by treating evaporated urine with alkohol, then with water, and afterwards with muriatic acid; the silica remains in the state of a grey powder, which may be fused with soda. As a minute portion of this earth exists in water used as drink, its presence in the urine probably originates in this source.

The action of re-agents on urine is instructive, as leading to a knowledge of the principles which exist in it, some of which could not otherwise be easily recognised. The principal accurate observations on the effects of these are those of Scheele, Cruickshank, Fourcroy, and Vauquelin.

The greater number of the acids produce little sensible effect upon it in the healthy state. The oxalic acid gives a precipitate, by combining with the lime of the superphosphate of lime which recent urine contains. If it contain benzoic acid, the muriatic acid is said to precipitate it. If it be much loaded with urée, nitric acid throws down a scaly precipitate of a pearly lustre. And, in certain morbid states, as in dropsy, the acids sometimes occasion a milkiness, or even a coagulation of the urine, from albumen being contained in it.

The fixed alkalis, added to urine, throw down a slight precipitate, which is phosphate of lime. About 2 grains, according to Cruickshank, are obtained from 4 ounces of urine. The watery solutions of lime, barytes, and strontites, produce more copious precipitates, as the salts they form with the phosphoric acid are insoluble. The fixed alkalis and lime disengage an ammoniacal odour, by decomposing the ammoniacal salts.

The nitrates and muriates of barytes, strontites, and lime, form precipitates, by decomposing the phosphates contained in urine. Four ounces of healthy urine, according to Cruickshank, yield with muriate of barytes a precipitate of 13 grains, consisting of phosphate of barytes, produced by the decomposition of the phosphates of soda and ammonia; a precipitate of 13 grains indicates a quantity of these, or of the combination of them, which has been named Microcosmic Salt, equivalent to 25 grains. The precipitate, however, formed by muriate of barytes, is, according to Berzelius, partly sulphate; and the quantity of sulphuric acid thus detected, he even finds to exceed that of phosphoric acid. The nitrates of silver, quicksilver, and lead, occasion a copious precipitation, the precipitate consisting principally of phosphoric acid, but partly also of muriatic acid, with the metallic oxide. If nitrate or acetate of lead be employed, the muriate of lead, it was remarked by Cruickshank, may be dissolved, by boiling in 18 or 20 times its weight of water, the phosphate of lead remaining undissolved, and thus, by weighing the original precipitate, and the loss it sustains in this operation, the quantities of phosphoric and of muriatic acids in the urine may be determined: an estimate, however, requiring correction, if sulphuric acid be also present. The fluate of lime may be discovered, according to Berzelius, by heating the precipitate from urine by lime-water with sulphuric acid, vapours being exhaled which corrode glass *; or by precipitating the urine by ammonia, collecting and calcining the precipitate, and treating it in like manner with sulphuric acid †.

Infusion of tannin produces a precipitate with urine: this has been supposed to be from its combination with gelatin: from the quantity of precipitate it has been estimated, that 4 grains of gelatin are contained in 4 ounces of healthy urine, and in certain morbid affections, especially where the digestive organs are impaired in their power, the quantity indicated by this test is considerable. Some chemists have supposed, that the precipitate tannin occasions may be owing to albumen; and Fourcroy and Vauquelin observed, in proof of the presence of this principle,

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* Philosophical Magazine, vol. xxviii. p. 307.

† Essay on Animal Fluids.

that flakes are formed in urine merely by heating it; but, with regard to this, there is some obscurity, for no coagulation is produced in it by acids or by alkohol, which there ought to be did it contain albumen.

It has been stated, in the preceding account of the analysis of urine, that when it is evaporated, so as to obtain the greater part of its saline ingredients by precipitation or crystallization, there remains a liquid of a dark colour, having the more evident urinous properties. This is principally a solution of the peculiar animal principle contained in urine. Obtained by evaporation, in intermixture with the saline ingredients, it was named, by the older chemists, Extract of Urine. It had been distinguished more particularly by Rouelle, and considered by him even as a distinct substance*. His observations, however, were neglected by chemists; and the existence of this principle may be said to have been re-discovered by Cruickshank †. He obtained it by adding to the extractive matter of urine, an equal weight of concentrated nitrous acid, diluted with an equal quantity of water; a violent effervescence, accompanied with heat, and disengagement of nitrous gas, takes place; when this has ceased, and the liquor become cold, a number of shining scales, or crystals, resembling the acid of borax, are deposited, which, when well dried on blotting paper, will be found to weigh from 5 to 7 drachms, from an ounce of the extractive matter, the proportion varying according to the quality of the extract, and the method of conducting the process.

" The figure of these scales," it is stated by Cruickshank, " is that of flat rhomboids; they have a smooth greasy feel when pressed between the fingers; are soluble in much greater quantity in hot than cold water, and also in some degree in alkohol; although repeatedly washed with this fluid, and dried on blotting paper, they still retain acid properties, and strongly redden the syrup of violets; they are readily taken up by the sulphuric and muriatic acids without commotion; but, with the nitrous acid, they produce a kind of effervescence, and appear to be in some measure decomposed; they combine with the mild alkalis with effervescence, and form very soluble neutral salts. Their solution in water does not precipitate lime-water, nor the muriates of lime or barytes, nor the nitrates of silver or mercury, nor has it any effect upon the sulphate of iron or acetate of lead; when thrown upon a red-hot iron, they melt and evaporate in white smoke, leaving a small quantity of a charry residuum; when exposed to an intense heat, they burn with a reddish flame, and a kind of detonation somewhat similar to the nitrate of ammonia. From these experiments, it would appear," he adds, "that this substance is an animal acid hitherto unknown, and whose basis exists in this extractive matter."

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* Journal de Medicine, 1773.

† Rollo on Diabetes, 2d edit.

Fourcroy and Vauquelin, in a dissertation on the urine of the horse *, prior to the publication of Cruickshank's experiments, had observed, that if to the liquor remaining after the separation, by evaporation, of the saline substances, and of the benzoic acid by muriatic acid, there be added nitric acid, a precipitation ensues of slender brilliant crystals, so as to form a concrete white mass, which became of a brown colour. This they considered as a principle before unknown: and, in a subsequent memoir †, they gave an ample detail of the facts they had discovered with regard to it. They gave it the name of URÉE. The following is the method by which they obtained it:

Urine is evaporated by a gentle heat, to the consistence of thick syrup. On cooling, it forms a confusedly crystallized mass, consisting of a mixture of its salts with the

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* Mémoires de l'Institut. National, tom. ii. p. 445.

† Ibid. tom. iv. p. 402.

urinary matter. Alkohol is poured on this mass, to the amount of four times its weight, in successive portions, heating them gently; the urée is dissolved, leaving undissolved the greater part of the saline matter; the solution is to be distilled by a gentle heat from a sand-bath; the alkohol passes over, impregnated with carbonate of ammonia, and animal matter. The distillation is continued until the liquor is of the consistence of syrup; in cooling, it crystallizes, affording quadrangular plates, crossing each other, of a brilliant yellowish colour. Or to the liquor diluted with water, nitric acid may be added; the usual scaly precipitate is formed; the nitric acid this contains is saturated by potash; the matter is then lixiviated with alkohol, which leaves the nitrate of potash undissolved, and by evaporation the same crystalline matter is obtained. This is the Urée. It exhales a strong urinous odour: it attracts humidity from the air, and forms a thick brown coloured liquid; and it dissolves rapidly in a small quantity of water, producing, during its solution, a sensible degree of cold: it is less soluble in alkohol, but its hot saturated solution in this fluid, gives, on cooling, crystals more readily than the watery solution. Its solution in water is of a brown colour; which, by dilution, passes through the different shades of orange, yellow, and lemon colour, so as to resemble urine in the various states in which it occurs.

From the detailed account which Fourcroy and Vauquelin have given of the chemical properties of urée, I give an abridged statement of the principal facts.

Exposed to heat in a retort it melts quickly, and a vapour is disengaged, which condenses in the neck into a crystalline deposite, having the appearance of benzoic acid. When this has ceased, carbonate of ammonia sublimes; and the sublimation of it continues, without interruption, to the end of the experiment; it is brown and of a very fœtid odour, but no oil is condensed, nor any watery liquor. The matter appears, at length, in a dry state, black, and covered with a white crust; this sublimes, and is muriate of ammonia. After exposure for two hours longer to the fire, the carbonaceous residuum gives, by lixiviation, a liquor containing prussic acid: it contains, too, muriate of soda, and a little muriate of ammonia. In burning it in an open fire, it disengages an ammoniacal odour, mixed with that of prussic acid. There remains an alkaline matter, amounting to about an hundredth part of the urée, apparently carbonate of soda. The benzoic acid, muriate of ammonia, and muriate of soda, obtained in this decomposition, these chemists considered as foreign to the urée; from the other products, it follows, that it is a compound of nitrogen, hydrogen, carbon, and oxygen; and the large quantity of ammonia which the analysis affords, proves that nitrogen is present in large proportion.

So susceptible is this principle of decomposition, and so liable are its principles to pass into those combinations which form ammonia and carbonic acid, that, by mere distillation with water, it is almost entirely converted into carbonate of ammonia. After three distillations Fourcroy and Vauquelin found, that the urée had afforded more than half its weight of carbonate of ammonia, and yet its power of yielding this product was not exhausted; for although, when diluted with a fresh quantity of water, it gave indications of the predominance of acetic acid, it lost this acidity in four or five days exposure to a temperature of 77°, and again gave an ammoniacal water by evaporation.

When left to itself in solution in water at a natural temperature, it passes into the acetous fermentation. The liquor, in a vessel imperfectly closed, becomes turbid, and aërial matter is disengaged, which extinguishes combustion; and, according to Gay Lussac, this is accompanied by an absorption of oxygen from the air: it acquires a sharp acidulous but fœtid odour. After this fermentation has ceased, if it be subjected to distillation, with the addition of sulphuric acid, acetic and benzoic acids are procured: the residuum contains sulphate of ammonia, and gives a precipitate of charcoal.

Urée, subjected to the action of acids, presents results different from those exhibited by any other animal principles, and which throw light on its composition.

Its solution in water, mixed with a fourth of its weight of sulphuric acid diluted, gives no effervescence. The mixture, heated until it boils gently, becomes covered with a layer of oily matter; a liquid is condensed of a yellow colour, and which is acid, from the presence of acetic and benzoic acids.

Nitric acid exerts on it a very peculiar action, altogether different from what would be expected from the known agency of this acid. Urée is extremely susceptible of decomposition; and nitric acid is, of any agent, that which acts with most energy in decomposing vegetable or animal substances; yet the urée is not decomposed by it, but seems to enter into combination with it. Cruickshank observed the precipitation of shining scales when nitric acid is added to urine concentrated by evaporation; and Fourcroy and Vauquelin found, that the same appearance is produced more distinctly with pure urée. When nitric acid is added to a solution of it in water, there is an instant deposition of crystalline plates, white, brilliant, and pearly, which augments so rapidly, that the whole mixture appears to be converted into this matter. This substance, heated gently, softens and melts like oil, an effervescence takes place, and it is in part converted into nitrate of ammonia. They regard it as a compound of urée and nitric acid.

When the nitric acid is concentrated, and surcharged with nitric oxide, and when the urée is concrete, the mutual action is attended with effervescence; nitric oxide, nitrogen, and carbonic acid gases, are disengaged, and there remains a yellowish concrete matter, with a few drops of a red liquid: if this residuum is heated, it detonates and inflames in the same manner as nitrate of ammonia. In this rapid action, the urée is decomposed. If the acid be diluted, and heat applied, it suffers decomposition more slowly; nitrogen, carbonic acid, and nitric oxide gases, are disengaged; and at length an elastic fluid similar to atmospheric air, having a sharp odour of prussic acid. When the heat is continued gently for a day or two, the matter at last becomes thick, and furnishing scarcely any considerable vapour, takes fire, with a violent explosion: there remains an oily carbonaceous matter, which gives to water an odour of prussic acid and ammonia, as well as the property of precipitating the solutions of iron blue. There is in this decomposition scarcely any production of that fat matter, of the bitter principle, or of the oxalic or saccholactic acid, which are generally the products of the action of nitric acid on animal matter; the whole consists in the disengagement of nitrogen, and the formation of carbonic acid, prussic acid, and ammonia,—a result which, as Fourcroy and Vauquelin observe, shews the predominance of nitrogen in the composition of urée; that, next to it, carbon is contained in largest quantity, and that the proportion of hydrogen is comparatively small.

Muriatic acid produces on this principle scarcely any effect, precipitating it only from its solution in alkohol in brown flocculi. Oxymuriatic gas transmitted through its solution is absorbed, the liquor becomes brown, flocculi of the same colour appear, which soon become yellow, and adhere to the sides of the vessel like a concrete oil.

Urée is soluble in alkaline solutions, but is also partially decomposed. When triturated with a solution of potash, an ammoniacal odour is exhaled. When the concrete urée is triturated with dry potash, an energetic action is manifested; the temperature rises; there is disengaged a much larger quantity of ammonia, and an oily-like matter appears on the surface. When heat is applied, the decomposition is rapid; pure ammonia, and carbonate of ammonia, are disengaged; the potash receives carbonic acid: a flocculent precipitate is deposited, having the properties of a concrete oil: and the liquor submitted to distillation, affords acetic and benzoic acids.

Urée has a singular effect on some of the neutral salts, —that of changing the form of their crystals. Muriate of soda crystallizes from urine, not in its usual form of cubes, but in octaedrons: and muriate of ammonia not in prisms, but in cubes. Fourcroy and Vauquelin found, that this depends on the action of the urée; since it equally happens when the salts are dissolved with pure crystallized urée in water; and the crystals, when freed from the urée by exposure to a red heat, crystallize in their usual form.

Tannin changes a little the colour of a solution of urée, but does not precipitate it; a character by which this principle is well distinguished from the albuminous or gelatinous matter so frequently associated with it.

Dr Prout, in a late investigation of the principles of urine *, has procured urée in what he considers as a state of purity, and has given a concise statement of its properties, which are in some respects different from those delivered by the French chemists. The following is his process to obtain it: " Fresh urine is to be evaporated to the consistence of a syrup, and to this, when quite cold, pure concentrated nitric acid is to be added by degrees, till the whole becomes a dark coloured crystallized mass, which is to be slightly washed with cold water, and suffered to drain. To this mass is to be slowly added a pretty strong solution of the sub-carbonate of potash or soda, till the whole becomes neutral, and the solution thus formed is to be carefully concentrated by evaporation and set aside, in order that the nitre formed may crystallize, and thus be separated. To the impure solution of urée left, animal charcoal is to be added in such quantity as to absorb the

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* Medico-Chirurgical Transactions, vol. viii. p. 526.

whole fluid, and form a thin paste, which may be suffered to lie for a few hours. Cold water is to be added to this paste, which separates the urée, and the colourless solution thus obtained is to be slowly evaporated to dryness at a low temperature. The resulting mass is then to be boiled in strong alkohol, which takes up the urée, and leaves the remainder of the nitre, and most of the other saline substances behind; and from this state of solution in alkohol, the urée may be readily obtained crystallized and pure, though it is generally necessary to repeat the process of crystallization from the alkohol two or three times."

Urée obtained by this process most frequently assumes the form of a four-sided prism. Its crystals are transparent and colourless, and have a slight pearly lustre. It leaves a sensation of coldness on the tongue like nitre. Its smell is faint and peculiar, but not urinous. It does not affect litmus or turmeric paper. It undergoes no apparent change on exposure to the air, except in very damp weather, when it slightly deliquesces, but does not seem to be decomposed. Exposed to a strong heat, it melts, and is partly decomposed, and partly sublimes apparently unaltered. The specific gravity of its crystals is about 1.350. Water at 60 dissolves more than its own weight of urée, and the solution exposed to the air for several months, underwent no change. Boiling water dissolves any quantity of it whatever, and the urée does not appear to suffer any change at this degree of temperature. Alkohol, (sp. gr. 816), at a mean temperature, dissolves about 20 *per cent.*, and at a boiling temperature, more than its own weight; and the urée separates on cooling in its crystalline form. It is very sparingly, if at all, soluble in sulphuric ether, or the essential oil of turpentine, though these fluids are rendered opaque by it. The pure fixed alkalis and alkaline earths decompose it, especially when heat is applied, and water present, the result is chiefly carbonate of ammonia. It unites with most of the metallic oxides; the combination with the oxide of silver is greyish, and detonates on being heated, and the oxide is reduced. It does not seem, however, to be alone capable of decomposing any metallic salt; but in order to effect the union, the aid of double affinity is necessary. It combines with nitric acid, and forms a crystallizing compound, but sparingly soluble in water, and which has been long known to chemists. It forms also a similar compound with oxalic acid. In neither of these compounds are the acids neutralized.

Fourcroy and Vauquelin, from the products of the decomposition of urée by heat, (page 547.) had inferred, that 100 parts of it are composed of nitrogen 32.5, carbon 14.7, oxygen 39.5, and hydrogen 13.3. From the period at which this analysis was executed, not much reliance could be placed on it. Dr Prout submitted urée to analysis by the method suggested by Gay Lussac, as applicable to animal substances, that of heating with oxide of copper. His results give as the composition, nitrogen 46.66, carbon 19.99, oxygen 26.66, hydrogen 6.66,—which, reducing these proportions to the standard of oxygen, as 10, give 1 equivalent or combining quantity of nitrogen, 1 of carbon, 1 of oxygen, and 2 of hydrogen. Berard by the same mode of analysis has given as the proportions, nitrogen 43.4, carbon 19.4, oxygen 26.4, hydrogen 10.8 *. Both agree in assigning a larger proportion of nitrogen to urée, than to any other animal principle.

As the precipitation of urée by nitric acid affords the most delicate and accurate mode of discovering this principle, Dr Prout has added the analysis of the compound which forms this precipitate, nitrate of urée, as he names it. It consists of 52.63 of urée, and 47.37 of nitric acid, 2 equivalent weights of the former, and 1 of the latter.

This principle being so uniformly secreted in considerable quantity, and discharged from the system, must be

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* Annales de Chimie et Physique, tom. v. p. 290.

subservient to some important purpose in the animal economy. Fourcroy and Vauquelin supposed, that it is designed to convey redundant nitrogen from the system, as the secretion of the bile discharges superfluous hydrogen, and the changes in the lungs, by respiration, perform the same office with regard to carbon. The difficulty, however, hitherto has been, rather to account for the origin of the nitrogen in the system of animals, than to provide for its discharge. Yet it is no doubt true, that nitrogen being contained in so large a proportion in urée, is proved to be uniformly discharged in considerable quantity; and this adds some force to the hypothesis, that by the series of chemical actions connected with animalization, it is formed or evolved, and that, in a system therefore liable to variations, we may look for a function by which its accumulation will be prevented. Berzelius, however, gives a different view of the subject. The elements of the blood are in part acidified in the kidneys; hence the redundance of saline matter, and in consequence of this, the other elements form the combination constituting urée, in which nitrogen is abundant, as it is not contained in any of the acids of the urine.

The tendency of this principle to pass to the state of ammonia, is probably frequently the cause of morbid changes to which the urine is liable; it may even sometimes contribute to the formation of urinary concretions; for if the excess of acid in the urine be saturated by the production of this alkali, the albuminous matter which the acid held in solution will be separated; and if a partial deposition of phosphate of lime or magnesia, or of uric acid, take place, as may happen from the same cause, the nucleus of a calculus may be formed. The cementing ingredient in many of these calculi appears to be albuminous matter, which is separated from urine whenever its acidity is neutralized; and the formation of such calculi may depend on some operation of this kind. The vitiated secretion of urée, it is immediately to be stated, there is reason to believe, gives rise to the production of diabetic sugar.

The predominance of nitrogen in the composition of urée, it is remarked by Fourcroy and Vauquelin, explains the great advantage derived from the intermixture of urine in the materials of nitre beds, in the production of nitre. And the production of ammonia, from the distillation of urine, a process carried on, in the large way, in the manufacture of muriate of ammonia, depends more on the decomposition of the urée, than on that of the ammoniacal salts which it contains.

There remains to be given, the chemical history of another substance contained in urine, and nearly peculiar to it, Uric Acid. The discovery of it we owe to Scheele. In analysing urinary calculi, he found them to consist principally of a substance sparingly soluble in water, but which, by boiling it in a large quantity of water, might be dissolved; it afforded a solution which reddened the more delicate vegetable colours, and from which, on cooling, the greater part separated in minute crystals. This he regarded as a peculiar acid; and he added the observation, that it is contained in urine, and frequently in considerable quantity, so as to be deposited as the urine cools *. Bergman had, about the same time, in analysing urinary calculi, observed this acid. It was made the subject of experiment by Dr Pearson †; several of its properties were pointed out by Fourcroy and Vauquelin: and Dr Henry has added to our knowledge of it in a dissertation ‡, from which I take principally the following facts. From being considered as the basis of urinary calculus or stone of the bladder, it received the name of Lithic Acid; a name improper, as it is

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* Chemical Essays, p. 199.

† Philosophical Transactions, 1798, p. 57.

‡ Manchester Memoirs, vol. ii. 2d Series.

not confined to these concretions, but is also contained in urine, while there are urinary concretions, in which no sensible quantity of it can be detected. As it is the acid peculiar to urine, the term Uric, which Dr Pearson suggested, is preferable.

There is a difficulty in procuring this acid pure; for as deposited from the urine, or as contained in urinary concretions, it is in a state of combination or mixture. The process given by Henry is, to dissolve a calculus, of that kind which consists chiefly of this acid, in a solution of pure potash. Muriatic or acetic acid is added to the solution, so as to be in excess; a white precipitate is thrown down, which is to be washed with tepid distilled water; and, more completely to remove any foreign acid, a few drops of water of ammonia are added to the water, with which it is first washed.

Uric acid obtained by this process, is in the form of a white powder, which yields easily to the pressure of the finger. It is altogether tasteless. It dissolves in 1150 times its weight of water at 212°, or in 1720 times at 60°. The solution, in hot water, deposites on cooling minute pellucid crystals. The infusion of litmus is reddened by this solution. Soap is decomposed by it, when it is digested with the acid in powder and as much water as is required to dissolve it; the oil is separated, and a milky like liquor produced. It decomposes the alkaline sulphurets, precipitating the sulphur; and it combines with the alkalis, earths, and metallic oxides, the alkaline properties being neutralized in the combination. These properties are sufficient to class it among the acids. Dr Pearson had inferred from his experiments, that it does not redden the vegetable colours, nor decompose soap: Observing farther, that it is tasteless, scarcely soluble in cold water, not capable of uniting with the alkali of carbonate of soda, potash, or ammonia, nor with the lime of lime-water, nor with oxide of mercury; and that its combination with caustic soda, resembles soap more than any compound salt known to consist of an acid and alkali, he inferred, that it ought rather to be regarded as an oxide than an acid *. But it obviously falls under the definition of an acid, though its acid powers are no doubt extremely weak. It is incapable of disengaging carbonic acid from the alkaline carbonates, nor is it dissolved by them: it acts with no energy on the metals, nor does it precipitate any earthy or metallic salt.

The combination of uric acid with the alkalis and alkaline earths are formed, by digesting them in hot water with a quantity of acid, more than sufficient for saturation, straining the solution, and evaporating it as far as may be necessary with a gentle heat. Dr Henry gives the following enumeration of the general properties of these urates. They are tasteless, and, in external appearance, can scarcely be distinguished from the acid itself. Exposed to the air, they undergo no change, neither losing nor attracting water. They are sparingly soluble in water. Urate of ammonia is the most soluble, and of it an ounce of water at 60 dissolves only 2 or 3 grains. The others, with regard to solubility, stand in the following order: urate of potash, of soda, of lime, of strontites, of magnesia, of alumina, and of barytes. If to the solution of any urate, any acid, the carbonic and prussic excepted, be added, the uric acid is precipitated in a white powder. The alkaline urates are also precipitated when the solution of any of them is mixed with the solution of any of the earthy muriates, nitrates, or acetates. The solutions of the urates cause precipitations in the solutions of the metallic salts, those of gold excepted, the precipitate consisting of the metallic oxide in combination with the uric acid. The urate of iron prepared in this way is of a reddish colour; that of copper a yellowish green; all the others are pale.

These salts are more soluble with an excess of base:

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* Philosophical Transactions, 1798, p. 27.

hence, when boiled with such an excess, they are dissolved in considerable quantity. The solutions of these sub-urates are precipitated by the acids; if a weak acid is employed in the experiment, as the prussic or carbonic, or if a small quantity of a stronger acid be added, the precipitate consists of the neutral urate; and the pure uric acid is not thrown down unless by a strong acid in large quantity.

Berard has inferred from the composition of the urates, that the acid is in a quantity which contains four times more oxygen than the base. Urate of barytes he finds to be composed of 61.64 of acid, and 38.86 of base: urate of potash of 70.11 of acid, and 29.89 of base.

Uric acid is decomposed by the more powerful mineral acids. Sulphuric acid heated on uric acid decomposes it: sulphurous acid is evolved, and there is a charred residuum. Muriatic acid has little effect upon it. Oxymuriatic gas decomposes it, and causes the formation of ammonia and of carbonic, malic, and oxalic acids. Nitric acid presents with it a singular result, which affords the character by which it can be most easily distinguished, that of giving a pink colour with it when heated. Scheele observed, that calculi composed of it, dissolved in nitric acid, formed a liquor which stained the skin of a red colour; and this solution, if neutral, assumed by evaporation a blood red colour. The same fact was observed by Bergman; he found the red colour to be assumed whenever the liquor was evaporated so far as to contain little nitric acid: it is communicated to water, but is destroyed by the acids, and by the alkalis *. This red or purple coloured matter, it is immediately to be stated, is, according to Dr Prout's experiments, a compound of a new acid with ammonia. By repeatedly distilling nitric acid from uric acid, the latter is entirely decomposed; nitric oxide gas is disengaged, and a portion of oxalic acid, according to Fourcroy, is formed.

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* Scheele's Chemical Essays, p. 200. 211.

Dr Pearson found, that carbonic acid gas, with nitrogen gas, were disengaged during the ebullition, a strong smell of prussic acid arose, and the residual fluid deposited crystals, which were nitrate of ammonia; the nitric acid, therefore, had, by parting with oxygen to the carbon of the uric acid, formed carbonic acid; and the hydrogen and nitrogen of the acid had formed ammonia, with which the redundant nitric acid had united *.

Uric acid is decomposed by heat: the products of the decomposition are water, carbonate of ammonia, carbonic acid, and carburetted hydrogen gases, prussic acid, and a matter which sublimes and condenses in a concrete form. The proportion of water is small; very little oil is formed; the proportion of prussic acid appears, from Austin's experiments, to be considerable †; and there remains a considerable quantity of charcoal, which, when burnt, affords little saline matter. From these products, and from those afforded by its decomposition by the acids, uric acid may be inferred to be a compound of carbon, hydrogen, nitrogen, and a small proportion of oxygen. Gay Lussac finds, that when it is decomposed by heating it with oxide of copper, the products are carbonic acid and nitrogen, in proportions which may be inferred to be two volumes of the former, and one volume of the latter. It consists, therefore, according to his view of the constitution of carbonic acid, of two volumes of carbon and one volume of nitrogen. This is the precise composition of cyanogen, the compound radical of prussic acid. In prussic acid, this radical appears to be acidified by a volume of hydrogen; and in uric acid it is probably acidified by a volume of oxygen ‡. Berard and Dr Prout have since executed its analysis in the same mode. The proportions of its ele-

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* Philosophical Transactions, 1793, p. 30.

† Treatise on Stone in the Bladder, p. 104.

‡ Annales de Chimie, tom. xcvi. p. 53.

ments assigned by the former are, nitrogen 39.16, carbon 33.61, oxygen 18.89, hydrogen 8.34,—those by the latter are, nitrogen 40.00, carbon 34.286, oxygen 22.857, hydrogen 2.857. The discordance between these in the quantities of oxygen and hydrogen, is probably to be ascribed to the presence or the abstraction of water. According to Dr Prout's analysis, the composition is 1 equivalent, or combining weight of nitrogen, 2 of carbon, 1 of oxygen, and 1 of hydrogen.

The sublimed matter from the decomposition of uric acid has attracted the attention of chemists, since it was observed by Scheele. Though at first brownish, it becomes white by a new sublimation: it has no smell, has a sourish taste, and is easily soluble in boiling water; it is also soluble, though sparingly, in alkohol: its solution does not precipitate lime-water. From these properties it seemed to Scheele to agree with succinic acid, while he appears to have also supposed, that it enters into the composition of the calculus. Hence, some chemists regarded this sublimate as the pure lithic acid. It is obviously different from the uric acid, which is obtained from calculi by solution in an alkali and precipitation by an acid; particularly in its sour taste, its greater solubility in water, and its being capable of being volatilized without decomposition. Neither is it acted on in the same manner by acids, and, in particular, it does not give a red colour with nitric acid. Dr Austin found, that if decomposed by heat, it affords ammonia, prussic acid, and nitrogen gas: a portion also sublimed, which, when again submitted to the same experiment, gave the same products, and this apparently without limitation, until its decomposition was complete *. Dr Pearson found that it reddened litmus, though its taste, instead of being sour, was only sharp and bitter: its solution in boiling water, gave by evaporation a deposite of

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* Treatise on Stone in the Bladder, p. 115.

white spiculæ: it was not soluble by boiling in muriatic or nitric acid, and with the latter, it left no red coloured matter, on the acid being evaporated from it. Sulphuric acid dissolved it, with the assistance of heat; it was also dissolved by boiling, by a solution of carbonate of soda, as well as by pure soda *. From its properties, Dr Pearson observes, that it appears to be analogous to benzoic acid; but the analogy is evidently very imperfect. Some farther observations have been made on it by Dr Henry, which agree with the preceding facts. He also found, that its solution by the alkalis is not precipitated by acids. It is soluble in cold as well as in warm water, and though its saturated solution reddens infusion of litmus, its acid power is so weak, that a drop or two of ammonia prevents this; nor does it effervesce with the alkaline carbonates. Its solution does not cause any precipitation from the earthy salts, as the solutions of the urates do; neither does it decompose the salts of copper, iron, gold, platina, or tin: from the nitrates of silver and of quicksilver, and from the acetate of lead, it throws down white precipitates. These results prove, that the acid existing in this sublimate is neither uric, succinic, nor benzoic acid; and it appears to be different from any known acid. It is contained in the sublimed matter combined with ammonia: from the products of its decomposition, it appears to be composed of the same elements as uric acid; and is probably formed from new combinations of these elements in the process by which it is obtained.

The action of nitric acid on uric acid has always attracted the attention of chemists, from the peculiarity of the product afforded by it,—the substance of a deep carmine colour, the production of which is the most characteristic test of the acid. Dr Prout has very lately discovered, that this substance is a compound of a new acid

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* Philosophical Transactions, 1798, p. 51.

formed in the process, with ammonia. I add the abstract which has been given of his experiments, read before the Royal Society of London.

This acid principle may be formed, not only from the action of nitric acid, but also that of chlorine and iodine on uric acid. As it possesses the remarkable property of forming beautiful purple compounds with the alkalis and alkaline earths, the name of Purpuric Acid has been given to it.

Purpuric acid may be separated from the purpuret of ammonia above mentioned, by the sulphuric or muriatic acids. It usually exists in the form of a light yellow or cream-coloured powder. It is exceedingly insoluble in water, and consequently possesses no taste, nor affects litmus paper, though it readily decomposes the alkaline carbonates by the assistance of heat. It is soluble in the strong mineral acids and in alkaline solutions, but not in dilute acids in general. In alkohol, it is insoluble. When exposed to the air, it assumes a purple colour, probably by attracting ammonia. Submitted to heat, it is decomposed, and yields carbonate of ammonia, prussic acid, and a little fluid of an oily appearance. Burned with the oxide of copper, it was found to consist of hydrogen 4.54, carbon 27.27, oxygen 36.36, nitrogen 31.81. The alkaline purpurates, as before observed, all form solutions of a beautiful purple colour. They are capable of crystallizing, and their crystals possess some remarkable properties. The purpurate of ammonia crystallizes in quadrangular prisms, which, when viewed by transmitted light, appear of a deep garnet red; but by reflected light, two of the opposite surfaces appear of a beautiful green, while the other two opposite surfaces appear of the natural colour. This curious property seems to be possessed by the other alkaline purpurates. The metallic purpurates are, in general, remarkable for their solubility and the beauty of their colours. The purpurate of zinc is of a beautiful gold yellow, the purpurate of tin of a pearly white, that of the other purpurates are more or less of a red colour *.

From the preceding history of urine, it appears that its composition is very complicated; it contains a number of ingredients, and these are often diversified. In the summary of its analysis by Fourcroy and Vauquelin, eleven substances are enumerated as constantly present in it, though variable in their proportions,—muriate of soda, muriate of potash, and muriate of ammonia; super-phosphate of lime, phosphate of magnesia, phosphate of soda, and phosphate of ammonia; uric acid and benzoic acid; a gelatinous or albuminous matter, and urée. The following has more lately been given as the entire composition by Berzelius,—water 933, urée 30.10, sulphate of potash 3.71, sulphate of soda 3.16, phosphate of soda 2.94, muriate of soda 4.45, phosphate of ammonia 1.65, muriate of ammonia 1.50, free lactic acid, and lactate of ammonia with animal matter and urée not separable from the preceding 17.14, earthy phosphates with a trace of fluate of lime 1.00, uric acid 1.00, silex 0.03, mucus of the bladder 0.32. The proportions of these are of course liable to be varied by circumstances affecting the secretion.

The composition of urine is considerably diversified by morbid states of the system. In the disease named Diabetes, saccharine matter is secreted by the kidneys, and often in large quantity; from the experiments of Cruickshank, it appears, that it has all the properties of vegetable sugar, while the proportions both of the saline ingredients and of the urée are much diminished. It had even been supposed that diabetic urine contains no urée, as it affords no scaly precipitate on the addition of nitric acid. But Dr Henry found, that the effect of this test is prevented by the saccharine matter †. Still the quantity

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* Annals of Philosophy, vol. xii. p. 68. † Ibid. vol. i. p. 27.

of urée is much diminished. This circumstance, as well as the theory of the production of sugar constituting this singular disease, have been well elucidated by Dr Prout, by a happy application of chemical analysis. He found diabetic sugar to be of the same composition as common sugar; and this he found to be composed of 39.99 of carbon, 53.33 of oxygen, and 6.66 of hydrogen, corresponding to 1 combining weight of each of these elements. From this, compared with the composition of urée, (page 553), it appears, that the weight of an atom or combining quantity of sugar, is just half that of urée; the absolute quantity of hydrogen in a given weight of both is equal, while the absolute quantities of carbon and oxygen in a given weight of sugar, are precisely twice those in urée *. The formation of sugar in diabetes probably depends therefore on a vitiated assimilation or secretion, whence the additional multiples of carbon and oxygen are communicated to urée. In dropsy, albumen is often contained in urine in such a quantity, that it bears a resemblance to the serum of the blood, and is coagulated by acids and by heat. In the dropsy, however, from diseased liver, it does not coagulate, but deposites a considerable quantity of a pink-coloured sediment, which Cruickshank found to consist of phosphate of lime, animal matter, to which its red colour was probably owing, and a little uric acid. Mr Rose discovered, that in inflammation of the liver, both acute and chronic urée is entirely wanting in the urine †. In fever, particularly at the crisis or abatement of the disease, a lateritious sediment is deposited, and nitrous acid, when added before the deposition takes place, gives a deep red tinge. In gout, the termination of the paroxysm is indicated by a deposition of a similar sediment. This sediment, Mr Cruickshank found to be composed of uric acid, phosphate

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* Medico-Chirurgical Transactions, vol. viii. p. 541.

† Annals of Philosophy, vol. vii. p. 56.

of lime, and some peculiar animal matter, but little soluble in water; and of these, the acid generally constitutes the smallest part *. In those spasmodic affections that attend some nervous diseases, the urine is transparent, abounding in saline, and having scarcely any extractive matter; similar appearances have been observed to precede delirium in fever. This state is discovered, by the infusion of oak-bark giving scarcely any precipitate with the urine, while acetate of lead produces a copious one. At the commencement of the paroxysm of gout, the urine, according to Berthollet, has a less proportion of acid than usual, while, towards its termination, it is increased. In rickets, according to Bonhomme, it is loaded with a large proportion of phosphate of lime, derived, probably, by absorption from the bones. Sometimes there is a deposite of phosphate of ammonia and magnesia, forming what is called White Sand. In other diseases, it exhibits other appearances:

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* Proust has affirmed, (Annales de Chimie, tom. xxxvi. p. 258.) that this sediment consists chiefly of a peculiar acid, which, from its colour, he has named Rosacic Acid, and which, he adds, is distinguished from uric acid, by its greater solubility in hot water, by not crystallizing so easily, and by giving a violet precipitate with muriate of gold. But these properties may arise from intermixture. Vogel has added some facts with regard to it. He procured it by digestion with alkohol, a white powder was left, which formed red scales when heated with nitric acid, and thus appeared to be uric acid. The alkohol saturated with red matter being evaporated, gave a red powder which he considered as pure rosacic acid. Its most striking properties were dissolving without effervescence in sulphuric acid, forming a liquor of a deep red colour, which loses its colour by dilution, and throws down a white powder, presenting all the characters of uric acid; and forming also with sulphurous acid a liquid of a very lively red colour. Except in these properties, it does not differ essentially from uric acid, and Vogel is disposed to conclude, that there is little distinction between them, (Philosophical Magazine, vol. xlvii. p. 228.).

sometimes it is viscid, sometimes white and milky; sometimes, again, of a dark colour, and extremely fœtid. These, and other states in which it occurs, have not been accurately chemically examined, though, in a medical point of view, they must afford important results.

It appears too, that the composition of the urine is influenced by substances received into the stomach. The flavour of several odorous substances is known to be perceptible in it soon after they have been swallowed. Saline matter appears to be peculiarly secreted; nitre, when it has been taken for some time in small doses, has been found so far to impregnate the urine, that paper dipt in it deflagrates weakly when kindled: alkalis can be given to that extent, that the urine becomes sensibly alkaline. And acids taken in certain quantities, so far influence the secretion, as to increase the precipitate of uric acid. The administration of the alkalis has an opposite effect: This also is the case, Mr Brande has shewn, with magnesia. The same substances, and also lime, he found favoured the deposition of the earthy phosphates of the urine; when an alkaline super-carbonate was given, a portion of the carbonic acid appeared to be secreted; and when water largely impregnated with carbonic acid was drunk, the urine yielded it copiously when heated, or when placed in the exhausted receiver of an air-pump *.

In different animals too, the urine varies considerably. In that of gramenivorous animals, the uric acid is wanting, while the benzoic is generally present in large proportion. Rouelle had examined that of the horse; he found it to afford no phosphorus; it contained sulphate and muriate of potash, carbonate and sulphate of lime, with the saponaceous extract, or urée, and a matter which rendered it viscid: and these results have been, in general, confirmed by the analysis of it by Fourcroy and Vauquelin;

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* Philosophical Transactions, 1810.

its ingredients, as determined by this analysis, being carbonates of lime and soda, muriates of potash and soda, benzoate of soda, and urée. That of the cow, according to Rouelle's analysis of it, gives results nearly the same, all its salts having a base of potash. That of the camel he found to contain carbonate, sulphate, and muriate of potash, with urée. Vauquelin has lately examined the urine of the lion, the tiger, and the beaver. The two first are perfectly similar, but differ from that of man in being alkaline, even when first discharged, from the presence of ammonia, in containing no uric acid, free or combined, in there being little phosphate of lime, which seems to be precipitated in the bladder, and hence their urine is usually turbid, and in containing little muriate of soda, but much sulphate of potash, and phosphates of soda and ammonia, with a redundance of urée. The urine of the beaver he found to be similar to that of herbivorous animals; it contained no uric acid or phosphoric salt, but urée, acetic, and benzoic acids, muriate of soda and sulphate of potash, carbonate of lime held dissolved by an excess of carbonic acid, and what are peculiar, carbonate and acetate of magnesia *.

THE concretions which sometimes form in the kidneys, or bladder, being derived from the urine, fall to be considered under its chemical history. The investigation of their nature is of importance in a medical point of view, as they give rise to one of the most painful diseases to which man is subject, and it is only by chemical researches that we can hope to discover the cause of their production, and of the means by which this may be counteracted, or by which, when they have been formed, they may be dissolv-

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* Nicholson's Journal, vol. xxxiv. p. 1.

ed. There remains, therefore, to be delivered the chemical history of URINARY CALCULI.

Though these concretions had long been attended to by chemists, nothing precise was known with regard to them previous to the discovery of uric acid by Scheele. From this discovery, it appeared that it forms the basis of them, and the knowledge of this fact regulated the subsequent investigations on this subject. Bergman confirmed the discovery of Scheele. Experiments continued to be repeated and diversified; whence it was discovered, that there exist other concretions besides those composed of uric acid; and a number of important results were established by the researches of Pearson, Wollaston, and Fourcroy and Vauquelin. Dr Wollaston, in particular, determined the composition of other species besides that composed principally of the uric acid; and detected the existence of various principles in urinary calculi which it had not been before known that they contained *. Fourcroy and Vauquelin gave a very elaborate memoir †, in which they described the diversified appearances these concretions present, either from chemical composition or mechanical structure. The result of all these researches is, that the following substances enter into the composition of urinary calculi: uric acid, urate of ammonia, phosphate of lime, phosphate of ammonia and magnesia, oxalate of lime, cystic oxide, silex,

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* Philosophical Transactions, 1797.

† { Mémoires de l'Instit. National. tom. ii. p. 112.
Annales du Museum National. tom. i. p. 93.

It is but justice to remark, that Dr Wollaston's dissertation was published in the Philosophical Transactions two years before the memoir by Fourcroy was read before the National Institute; and that it anticipates nearly every thing which the French chemist announced as discoveries on this subject.

and animal albumen, these principles being in greater or less proportion in different varieties, so as to give rise to some difficulty in adopting an arrangement with regard to them.

The calculi which were first properly analysed, are those composed of uric acid. They are of a brown or yellowish colour, smooth on the surface, and with a texture compact or radiated; are soluble in alkaline solutions, and give a red colour when treated with nitric acid.

Another calculus had been observed, white, of a lamellated texture, and fusible before the blowpipe into an opaque white glass. This Dr Wollaston found to be composed of phosphate of magnesia and ammonia, and phosphate of lime.

Another had been distinguished by surgeons by the name of the Mulberry Calculus, from its dark colour and irregularly knotted surface, bearing some resemblance to that fruit; and it had been observed, that this is little affected by an alkaline solution. Dr Wollaston found it to consist of oxalate and phosphate of lime.

He lastly discovered one consisting entirely of phosphate of lime, of a pale brown colour, so smooth as to appear polished, composed of concentric crusts, and soluble, though slowly, in nitric or muriatic acid.

These form four species, under which he arranged urinary calculi: 1*st*, The uric acid concretion: 2*d*, The fusible calculus, formed chiefly of phosphate of ammonia and magnesia: 3*d*, What he named the Bone Earth Calculus, as composed of phosphate of lime, which forms the basis of bone; and, 4*th*, The mulberry calculus, or oxalate and phosphate of lime. To these may be added another, which he has since discovered, the Cystic Oxide Calculus. The arrangement of urinary concretions by Fourcroy and Vauquelin is more minute and complicated, as they form a number of distinctions from mechanical structure and intermixture. But in a chemical classification these can scarcely be regarded, and the classification of Dr Wollaston is sufficiently precise, placing under each species those calculi in which there is mechanical intermixture, according to the predominant ingredient.

1. Uric Acid Calculus. Calculi of this kind are usually in fine and close layers, fibrous or radiated, smooth on the surface, though sometimes a little rough, of a yellowish or brown colour, similar to that of wood. They are rather brittle, and have a specific gravity, varying from 1.276 to 1.786, but usually above 1.500. They blacken without melting on burning fuel; exhale an odour similar to that of bone burning, and give by distillation, ammonia and prussic acid. They are insoluble in cold water, but when in powder, and the water is at the temperature of 212°, a solution is obtained, and small crystals are deposited on cooling. They are soluble in the cold in a solution of pure potash or soda, and from the solution a precipitate of a fine white powder is thrown down by acids. Lime-water dissolves them, but more sparingly. In solutions of the alkaline carbonates, they remain, according to Scheele, unchanged: according to the experiments of Dr Egan, however, they are dissolved even by weak solutions, and also when the alkali is super-saturated by carbonic acid *. The weaker acids have no effect on them. Even the muriatic acid does not dissolve them. Nitric acid, however, assisted by heat, acts upon them, and produces the deep red colour which is so characteristic of uric acid. In many of them the uric acid appears to be nearly pure: in others there is an intermixture of other ingredients, particularly of phosphate of lime, and phosphate of magnesia and ammonia; and in almost all of them a portion of animal matter, whence the smell they emit in burning, and the loss observed in their analysis.

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* Transactions of the Irish Academy, 1805; or Philosophical Magazine, vol. xxiii. and xxiv.

A Calculus of Urate of Ammonia has been described by the French chemists, which has some resemblance in structure to that composed of pure uric acid, only the layers are less sensibly striated: its colour is lighter, often inclining to grey or greyish white: the surface is smooth, sometimes brilliant and crystalline, and sometimes the external layer is pure uric acid. The specific gravity is from 1.225 to 1.720. The distinguishing chemical characters assigned to calculi of this kind are, solubility in alkaline solutions, and their giving out, while they dissolve, a strong ammoniacal odour, two characters which are not found together in any other species. They are also soluble alone in hot water, and are rendered more soluble by an excess of ammonia. All the acids abstract their base, and reduce them to the state of uric acid. Heated by the blowpipe, they exhale ammonia, and then present the same appearances as the uric acid calculus. There is some doubt with regard to this calculus. Dr Wollaston, Mr Brande, and Dr Marcet, have never been able to discover it; and Mr Brande has supposed, that the ammonia which it is said to yield might be derived from phosphate of ammonia and magnesia, mixed intimately with uric acid*. At the same time, there is certainly nothing to preclude the production of urate of ammonia.

2. Calculus of Phosphate of Magnesia and Ammonia. This substance scarcely ever forms a calculus alone: it is either discharged in the form of a white sand, which consists of very minute crystals, or it forms layers, which alternate with other ingredients, or cover a nucleus of uric acid. It is distinguished when in these layers, or when predominant in a mixed calculus, by its lamellated structure, its white colour, and the closeness and fineness of its texture; it is soft and smooth to the touch, is easily sawed through, and gives a fine light powder of a brilliant white-

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* Philosophical Transactions, 1808.

ness. It has a taste mild and sweetish, without feeling dry like phosphate of lime. With this substance, however, it often occurs in intimate intermixture, and the two modify the properties of each other, particularly with regard to fusibility, so that this mixed calculus melts easily before the flame of the blowpipe into a white enamel, and hence is denominated the Fusible Calculus, which, next to the uric acid calculus, is the most common. It is usually white and friable, laminated in its texture, and sometimes studded with small crystalline grains of the phosphate of ammonia and magnesia. When placed on burning fuel, it blackens and exhales an empyreumatic ammoniacal odour, and melts when the heat is raised. It dissolves in water sparingly, still, however, so far, that when the water is boiled on it and evaporated, it deposites minute crystals on cooling. It dissolves easily in the acids, even those that are weak; when immersed in dilute muriatic acid, both the phosphate of lime, and the phosphate of ammonia and magnesia, are dissolved; and there remains a membranons matter in light flakes, consisting of the albumen mixed with it, with sometimes a little uric acid. Diluted acetic acid dissolves the triple phosphate alone. The fixed alkalis disengage ammonia, combine with the acid, and separate the magnesia and lime. Ammonia has little effect on it. By subjecting calculi, into the composition of which it enters, to the successive action of these re-agents, they may be analysed. Thus, according to Dr Wollaston's method, the phosphate of magnesia and ammonia is dissolved by distilled vinegar in the cold, with scarcely any phosphate of lime: muriatic acid poured on the residuum, dissolves the phosphate of lime: and a fixed alkaline solution takes up the uric acid. The proportions of phosphate of ammonia and magnesia, and phosphate of lime, are very various, and the fusibility of the calculus varies according to the intermixture.

3. Calculus of Phosphate of Lime. From the observa-

tions of Wollaston, it appears, that this substance sometimes composes an entire calculus, though more generally it is mixed with other ingredients, particularly with uric acid, and with phosphate of magnesia and ammonia. In the first case, the calculus is of a pale brown colour, and so smooth as to appear polished; when sawed through, it is found regularly laminated, and the laminæ, in general, adhere so slightly, as to separate with ease into concentric crusts. It dissolves entirely, though slowly, in muriatic or nitric acid. Exposed to the flame of the blowpipe, it is first slightly charred, but soon becomes white, retaining its form, until urged with the utmost heat from a common blowpipe, when it may be fused. It appears to be more fusible than the phosphate of lime, which forms the basis of bone, which Dr Wollaston supposes owing to the latter containing a larger proportion of lime *. The calculi in which phosphate of lime alone exists are rare, but those in which it is mixed with other ingredients, particularly phosphate of magnesia and ammonia, and uric acid, are more numerous, and are diversified in the appearances they present. According to Fourcroy and Vauquelin, it appears in these either under the form of layers, friable, breaking into scales under the saw, of a greyish white colour, dull, and without any lamellated structure; or, instead of layers, it presents incoherent grains, friable, and with little induration; and, by this dry and earthy appearance, and the dulness of its colour, it is distinguished from the phosphate of magnesia and ammonia. Calculi of either kind are charred by being heated; calcined to whiteness, they do not afford lime. They are dissolved by the acids even when much diluted, and the phosphate of lime is precipitated by the alkalis. They are not affected by alkaline solutions. From their state of intermixture, however, they are liable to variations both in their physical properties and

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* Philosophical Transactions, 1797, p. 395.

chemical characters. And the different ingredients can be recognized with certainty only by analysis.

4. Calculus of Oxalate of Lime. This species has been long known by the name of the Mulberry Calculus, from its colour and its rough pointed surface: the composition of it was discovered by Dr Wollaston. It is of a dark brown colour externally, frequently grey within: its surface is usually uneven, presenting tubercles more or less prominent, frequently rounded, sometimes pointed, and either rough or polished; sometimes, however, it is perfectly smooth, and of a pale yellow colour: it is very hard, difficult to saw, and appears to consist of successive unequal layers: it is also the heaviest of the urinary concretions. With regard to chemical characters, it is less affected by the application of the usual re-agents than any other calculus. The pure alkaline solutions have no effect upon it, and the acids dissolve it with great difficulty. When it is reduced, however, to fine powder, both muriatic and nitric acid dissolve it slowly. The solutions of the alkaline carbonates decompose it, as Fourcroy and Vauquelin have observed; and this affords the easiest method of analysing it: the calculus in powder being digested in the solution, carbonate of lime is soon formed, which remains insoluble, and is distinguished by the effervescence produced by the addition of weak acetic acid, while there is obtained in solution the compound of oxalic acid with the alkali of the alkaline carbonate: from this the oxalic acid may be precipitated by acetate of lead or of barytes; and this oxalate thus formed may be decomposed by sulphuric acid. Another method of analysing this calculus is by exposure to heat: its acid is decomposed, and by raising the heat sufficiently, pure lime is obtained, amounting to about a third of the weight. This species, it is remarked by Fourcroy and Vauquelin, contains more animal matter than any other, from which its colour appears to be derived, and which gives to it also its hardness and dense aggregation:

this animal matter appeared to be a mixture of albumen and urée. Dr Wollaston found it to contain usually a little uric acid, and phosphate of lime.

5. Cystic Oxide Calculus. This is composed of a substance discovered by Dr Wollaston, to which he gave the name of Cystic Oxide. The calculus bears some resemblance to that composed of phosphate of magnesia and ammonia, but is more compact; and instead of the whiteness and opacity of the other, it has a yellowish semi-transparency with a glistening lustre. It emits before the flame of the blowpipe a very peculiar fœtid smell. It is acted on by the usual re-agents, being dissolved by the stronger acids, by the alkalis, and by lime-water, and by the carbonates of potash and soda. Its combinations with acids may be made to crystallize, forming slender spiculæ, radiated from the centre, which dissolve readily in water. The muriatic combination is decomposed by the heat of boiling water, and the acid is expelled: the salt with nitric acid does not yield oxalic acid, and does not acquire a red colour when heated. From the ready disposition of this substance to unite both with acids and alkalis, Dr Wollaston concluded that it may be ranked as an oxide *.

Dr Marcet, in his late treatise on Calculous Disorders, has noticed another calculus, composed of a substance which had not been before observed, and to which, from its characteristic property of forming a yellow coloured matter when acted on by nitric acid, he gives the name of *Xanthic Oxyd*. A single specimen only has been procured. It was of a small size; its texture compact, hard, and laminated; surface of a reddish colour: before the blowpipe it splits, becomes black, and is consumed: when reduced to an impalpable powder, and boiled in water, it is dissolved, and the solution reddens litmus slightly; it is insoluble in alkohol or ether; it is dissolved by the alkalis and alkaline sub-carbonates, but not by the bi-carbonates; it is very sparingly soluble in acetic acid, and insoluble in oxalic acid. The mineral acids dissolve it, though sparingly: when its solution in nitric acid is evaporated to dryness, the residue assumes a bright lemon colour; the matter is partly soluble in water, to which it communicates its colour; the addition of an acid removes the yellowness, but if potash be added to the yellow substance, it becomes of a deep red, which by dilution with water, however, becomes again yellow. These properties seem sufficiently characteristic, to establish this as a peculiar substance.

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* Philosophical Transactions, 1810.

Dr Marcet has observed another urinary calculus, of a colour and consistence similar to bees wax, somewhat elastic, and of a fibrous texture; and which he found to have all the chemical properties of fibrin. He distinguishes it by the name of Fibrinous Calculus.

It appears that carbonate of lime sometimes enters into urinary calculi. Fourcroy and Vauquelin found in two calculi of six hundred which they analysed, siliceous earth: it was mixed with uric acid and urate of ammonia in the nucleus and internal layers. As silex, from the experiments of Berzelius, appears to exist in the urine, it probably is not unfrequently an ingredient in urinary calculi, though, from the minuteness of its quantity, it may not have been perceived. Iron, too, has been sometimes discovered in these concretions*, and as a trace of this metal has sometimes been found in urine, a similar remark may perhaps be applied to it.

There is present in the calculi of every species, as has been already remarked, a portion of animal matter: it is it, according to Fourcroy and Vauquelin, which is the source of their colour and induration; and it appears to have an important share in their formation: it is found even in those which appear most white and crystalline, and in others is contained in large quantity: it often remains in flocculi when the other ingredients have been dissolved by re-agents: they supposed it to be analogous to albumen, with the exception of that in the mulberry calculus, which appears to approach to urée. It seems in general to be rather the mucus of the bladder. Berzelius has remarked, that the mucus suspended in the urine, in its deposition as it cools, seems to promote the crystallization of uric acid, the minute crystals of the acid not forming so readily when this mucus is not present. And hence the probable conjecture which he suggests, that if from long retention of the urine, or from confinement to the horizontal posture, the mucus in the urine (which is of greater specific gravity, and therefore slowly subsides from it) accumulate, it may give rise to the formation of a concretion *. It may be owing even to this, that the disease commences so frequently in infancy, as there is reason to believe it does.

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* Annals of Philosophy, vol. vii. p. 57.

Such are the ingredients in urinary calculi, and the species under which they may be arranged. It is only farther to be remarked, that they are much diversified by mechanical intermixture, layers of these ingredients often alternating. Those intermixtures which have been most frequently observed, and which are pointed out by Fourcroy and Vauquelin, are, 1*st*, The mixture of uric acid and of earthy phosphates; the former generally forming the nucleus, and the phosphate of lime, and phosphate of magnesia and ammonia, being either intermixed or in alternate layers. 2*dly*, Those of urate of ammonia and earthy phosphates, the nucleus of this variety being commonly urate of ammonia, and the layers being phosphate of lime and phosphate of magnesia and ammonia mixed with it, and, at the same time, sometimes alternating with fine layers of it, or even of uric acid. 3*dly*, That of oxalate of lime and of uric acid, the first generally occupying the centre. 4*thly*, That of oxalate of lime and earthy phosphates; the first forming the nucleus, the second enveloping it in different layers: And, *lastly*, The alternation of uric acid alone or mixed with urate of ammonia, with oxalate of lime and earthy phosphates; the nucleus being oxalate of lime, the intermediate layers uric acid or urate of ammonia, and the exterior, earthy phosphates intermixed with each other and with uric acid. Of all the urinary concretions, those of uric acid have been supposed to be the most common. Of 200 specimens which Dr Pearson analysed, not more than six did not contain uric acid, though he found its proportion very various. And Fourcroy and Vauquelin found, among 600 calculi, more than 150 composed of pure uric acid. The observations of Mr Brande, however, are at variance with this. Of the collection of calculi in the Hunterian Museum, he found 16 were composed of uric acid, 45 of uric acid with a small proportion of phosphates, 66 of phosphates with a small proportion of uric acid, 12 of phosphates entirely, 5 of uric acid with phosphates and nuclei of oxalate of lime, and 6 chiefly of oxalate of lime. Of 181 specimens examined by Dr Marcet, he found 66 of uric acid, 49 of the fusible calculus often mixed with triple phosphate, 4 of phophate of lime, pure, or alternating with triple phosphate, 41 of mulberry calculus, 19 calculi in alternating layers, chiefly of uric acid and the matter of mulberry calculus, and 2 of ingredients intimately mixed.

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* Annals of Philosophy, vol. ii. p. 419.

It appears from Mr Brande's observations, that calculi formed in the kidneys are almost always of uric acid; the more rare calculus of oxalate of lime appears to be formed in the same organ. Calculi composed in whole or in part of phosphates, seem to be principally formed in the bladder. Hence, too, the nucleus of mixed calculi is almost uniformly either uric acid, or oxalate of lime, while the superadded layers consist of phosphates pure or alternating with uric acid. The nucleus itself has probably been formed in the kidneys, and the additional matter deposited in the bladder. Where the disposition, it is remarked by Mr Brande, to form uric acid in the kidneys is great and permanent, the calculus found in the bladder is principally composed of uric acid, (the urine having been so much impregnated with it); but where this disposition is weak and of short duration, the nucleus only is uric acid, and the bulk of the stone is composed of the phosphates. Where the increased secretion of uric acid returns at intervals, the calculus is composed of alternate layers of uric acid and the phosphates. And when a constant increased secretion of uric acid is going on from the kidneys, only in small quantity, it will be more uniformly mixed with the phosphates deposited in the bladder *.

Fourcroy and Vauquelin have given a very good summary of the chemical phenomena presented by re-agents on the usual ingredients of urinary calculi, by which they may be recognised. In applying a pure alkaline solution, five appearances present themselves, from which indications may be drawn: 1*st*, The alkali may dissolve the calculus entirely, and without causing any evolution of ammonia; in which case it may be inferred, that it consists of uric acid. 2*dly*, The solution may be complete, but accompanied with a strong ammoniacal odour: the calculus then consists of urate of ammonia, without any earthy phosphate, or at least of uric acid, with an intermixture of ammoniacal salts. *3dly*, The alkali may dissolve only a part of the calculus in powder, without causing any exhalation of ammoniacal odour; in this case there is indicated a mixture of uric acid and phosphate of lime. *4thly*, The alkaline ley, in effecting a similar partial solution, may at the same time disengage ammonia; in this case there are indicated uric acid which has been dissolved, and phosphate of magnesia and ammonia which has been decomposed; the undissolved portion must contain the magnesia, which may be discovered by solution in weak acetic acid, and precipitation by potash; while the alkaline ley contains the phosphoric acid, which may be precipitated by lime-water, and the uric acid, which may be thrown down in a crystalline form by muriatic acid. *5thly*, There is present sometimes, in the treatment of the calculus by the alkaline ley, an evolution of ammonia, while no uric acid can be precipitated from the solution by the addition of the other acids; indicating of course the presence only of phosphate of magnesia and ammonia, mixed generally with more or less phosphate of lime. The oxalate of lime is not dissolved by the alkaline solution, but by the alkaline carbonates, producing carbonate of lime, by which it may be recognised, as well as by furnishing lime, when the calculus has been urged with a strong heat *.

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* Oxalate of lime is rather a singular ingredient to be found in urinary concretions; nor has any theory been proposed to account for its origin. It is probably to be accounted for on the relation which has been pointed out (page 564.) between urée and saccharine matter, that in the latter there are two proportions of carbon and oxygen, to one in the former, the proportion of hydrogen in each being the same. Sugar is convertible by a change in the proportions of its elements into oxalic acid; it is conceivable, therefore, that urée may, by a farther change corresponding to this relation, yield oxalic acid, as a consequence of morbid secretion. And whenever oxalic acid is formed in the secretion of urine, it will attract the lime of the phosphate of lime which is present, and form oxalate of lime, the insolubility of which will cause its precipitation, and may give rise to the nucleus of a concretion.

I add the following abstract of an excellent summary by Dr Marcet, of the general methods of determining the nature of the different species of calculi †. When a calculus is of a brownish colour, compact, rather hard, smooth or nearly so, and of the shape of a flattened oval, there is great probability of its being of the uric acid kind. If a fragment not larger than a pin's head is exposed to the flame of the blow-pipe, if this acid be its principal ingredient, the fragment blackens, emits a smoke having a strong and characteristic odour, and is gradually consumed, leaving a minute quantity of white ash, which is usually alkaline. The uric acid may be also recognised, by being dissolved by caustic potash: if a minute portion scraped off the calculus, be heated gently in a watch-glass, with a few drops of the alkaline liquor, it is immediately dissolved, leaving a residue more or less considerable, according to the proportion of the other substances contained in the calculus; and by adding to the solution any acid, a white precipitate of uric acid is thrown down. Lastly, if to a small particle of it a drop of nitric acid be added, and heat applied, it assumes on becoming dry a beautiful pink or carmine colour, which it communicates to water by solution.

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* Mémoires de l'Instit. National, tom. iv. p. 125. 150. 157.

† Essay on Calculous Disorders, p. 112.

The indications by which the phosphate of lime calculus is identified are, that before the flame of the blowpipe it first blackens, but soon becomes perfectly white, retaining its form, and not exhibiting any appearance of fusion, unless the most intense heat be applied: and that when pulverised it is readily dissolved by dilute muriatic acid, and if there is not a great excess of acid, a precipitate is thrown down by oxalate of ammonia.

The ammoniaco-magnesian phosphate is discernible by its whiteness, and its crystalline sparkling appearance. If exposed to a gentle heat, or treated with a few drops of caustic potash, ammonia is exhaled. If urged by the flame of the blowpipe, the phosphate of magnesia remaining after the expulsion of the ammonia is opaque, and undergoes only an imperfect fusion. This calculus dissolves easily in dilute acids; and on adding an excess of ammonia to the solution, the white shining precipitate of the triple phosphate is formed.

The fusible calculus is distinguished by melting easily before the flame of the blowpipe into a globule of a pearly appearance. It is readily dissolved by dilute muriatic acid; the lime may be precipitated from the solution by oxalate of ammonia, and the triple phosphate of magnesia and ammonia is thrown down by adding ammonia in excess.

Of the mulberry calculus, the most obvious chemical character is to swell out, when exposed to the heat of the blowpipe, into a kind of white efflorescence; this is caustic lime, (the oxalic acid being decomposed by the heat), and is easily recognised by rendering green moistened paper stained with the colour of violet, or rendering brown in like manner the colour of turmeric. If it has a mixture of uric acid, a stronger heat is required to produce the effect, than when it consists only of oxalate of lime.

The cystic oxide calculus is recognised by its unstratified and homogeneous structure, and its peculiar smell when heated; and its great solubility both in acids and alkalis is a certain criterion of it.

The investigation of the composition of urinary concretions leads to the interesting question, how far their solution in the bladder may be practicable, and if it is, by what agents it may be best effected?

Experience has established the advantage derived in calculous affections from the use of alkaline remedies. Where the pure alkali is used, and the calculus consists chiefly of uric acid, a real solvent power may be exerted; for it has been proved, that the alkali is secreted by the kidneys, so as to render the urine alkaline, and capable of acting on the calculus out of the body. Yet the solvent power is very inconsiderable, and the remedy proves so irritating, when taken to any considerable extent, that the solution of a calculus even of a small size can scarcely be expected. The pain and irritation which attend the disease, however, are considerably alleviated by the habitual use of alkalis, and this even when super-saturated with carbonic acid, partly perhaps from the solvent power of the alkali on the uric acid, and partly from its neutralizing the acidity of the urine, which is thus rendered less irritating, and the tendency to a deposition of uric acid is diminished. It has accordingly been found, that under the use of alkaline remedies, the sediment of uric acid from the urine rapidly diminishes.

So far the alkalis may act as palliatives, while there is no reason to believe that they can be given to that extent to exert an actual solvent power. There is, besides, an effect which may attend their continued use, which Mr Brande pointed out. The phosphates of lime and magnesia are held in solution in urine chiefly by its excess of acid; if this be saturated by the use of an alkali, although the deposite of uric acid may be checked, that of the phosphates will be favoured, and it appears that it is principally from the deposition of these that a calculus in the bladder increases in size. Much care, therefore, is necessary to regulate the administration of the alkalis, according to the tendency of the urine to acidity, and particularly not to carry them to excess, so as to cause the deposition of the earthy phosphates. And it is not improbable, as Mr Home has suggested, that the appearances on the surface of some calculi, their porosity and softness, which have been observed after the long-continued use of alkalis, and regarded as proofs of their solvent power, have arisen from this deposition of the ammoniaco-magnesian phosphate *.

Lime, under the form of lime-water, has been employed as a solvent; and some experiments by Dr Egan have shewn, that lime-water acts with more energy than an alkaline solution of similar strength, in destroying the aggregation of urinary concretions; an effect which I have also observed, in a comparative trial which these experiments led me to make. In a dilute solution of pure potash, a calculus of the uric acid kind was soon in part dissolved, but the remaining calculus preserved its aggregation, the external layer having been merely removed; while

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* Philosophical Transactions, 1808.

a calculus of a similar kind, and discharged from the same person, immersed in lime-water, became in a few days white and spongy, and at length presented a kind of loose scaly appearance, while the least touch made it fall down. The lime probably operates more upon the animal matter, which serves as the cement or connecting substance, than upon the uric acid. If lime, when received into the stomach under the form of lime-water, can be secreted by the kidneys, as the alkalis are, it might be inferred from these observations, to be superior as a solvent. But, considering the sparing solubility of lime, and the small quantity of it that can be brought to the kidneys, the possibility of its secretion may be doubted: and if it were secreted, it might combine and form an insoluble compound with the phosphoric acid, or with the carbonic acid contained in urine. Some advantage might be derived from its powerful action on the animal matter of the calculus, if its saturation by the acid of the urine were prevented by the joint administration of an alkali. The celebrated Stephen's remedies, it may be remarked, were a combination of this kind.

Mr Home, concluding that calculous affections might be obviated by the introduction of substances into the stomach, which would prevent the formation of uric acid, thought of employing magnesia for this purpose; and the practice appears to be attended with much advantage: the exhibition of magnesia in small doses being found, in cases where there was an increased formation of uric acid, to diminish it in a much greater degree than had been effected by the use of the alkalis. It must also be less liable to cause the deposition of phosphates from the urine, owing to its insolubility, whence it is not liable to be secreted by the kidneys. And it has the important advantage of being perfectly mild in its operation *. It appears, however, from some subsequent cases †, that it may be used in ex-

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* Philosophical Transactions, 1810. † Ibid. 1813.

cess so as to cause the deposition of the earthy phosphates, no doubt by diminishing the natural acidity of the urine. Still it must be less liable to do so than alkalis; and a little attention may guard against any injurious effect. It is not less necessary to guard against its accumulation in the intestines.

Those calculi which are composed of oxalate of lime, phosphate of lime, or phosphate of magnesia and ammonia, not being soluble in alkalis, it has been supposed that their solution, if attempted, must be by the action of weak acids; and there are cases on record in which the pain from urinary calculus has been relieved by the use of vegetable acids, as that of lemons. It may be doubted, however, if the use of any acid can be carried to that extent to communicate to the urine a solvent power. And with regard to this there would be a difficulty similar to that which attends the use of alkalis; for though the acid might remove the phosphates, or prevent their deposition, it would favour that of the uric acid, and the concretion might increase therefore from this cause. Nor can we ever hope, by an alternate exhibition of acids and alkalis, to adjust them to each other, so as to obtain their solvent effects without these counteracting results. Acids, however, may be so given as to correct the tendency to the deposition of the earthy phosphates where it exists, and those which are weak may be preferred. Water impregnated with carbonic acid, was at one time employed; and Mr Brande has stated, that water with this impregnation in some cases produced so far an effect, that while it was administered, the phosphates were voided in solution, but when it was left off, they were discharged in the form of fine sand. This renders it proper, perhaps, when employing alkalis, to use them rather in the state of super-carbonate, than in their pure form, as, if given even in excess, they will in the former state be less liable to occasion the deposition of the earthy phosphates. It appears, also, that the vegetable acids, the tartaric, and especially the citric, are less liable to cause the deposition of uric acid, than the mineral acids, while they equally prevent the separation of the earthy phosphates. The carbonic acid is peculiarly adapted to those cases where the bladder is more than usually irritable *.

Fourcroy and Vauquelin have proposed †, that the solution of urinary concretions should be attempted by the injection of the proper solvents into the bladder largely diluted. From the extreme irritability of the bladder, however, with regard to every fluid but that which it usually contains, there can be little doubt but that this project is impracticable.

The preceding history of urinary concretions applies to those formed in the human system. They are sometimes found in other animals; and calculi of this kind from the dog, the horse, the hog, the ox, and other quadrupeds, have been examined by Dr Pearson, Fourcroy and Vauquelin, and Mr Brande ‡. They have presented the singularity, that the uric acid is wanting; they consist generally of phosphate and carbonate of lime with animal matter.

SECT. IX.—OF SYNOVIA.

THIS name is given to the liquor found within the capsular ligaments of the joints, which is designed to facilitate the motion of the articulated bones. It was submitted to

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* Philosophical Transactions, 1813.

† Mémoires de l'Institut. National. tom. iv. p. 147.
Fourcroy's System, vol. x. p. 551.

‡ Pearson, Philosophical Transactions, 1798, p. 59.
Fourcroy, Annales du Museum National, tom. iii. p. 504. tom. iv. p. 329.

chemical examination by Margueron, from whose memoir[*] the following account is taken.

It is viscous, transparent, and of a greenish colour: when withdrawn from its capsule, it becomes gelatinous; but after some time, it loses this, and deposites a fibrous elastic matter. It mixes with cold water by agitation, and renders it viscous: when the mixture is heated, it becomes milky, and pellicles are formed, but still remains viscous.

Acids added to synovia, produce a flocculent precipitate, which is soon re-dissolved. When the stronger acids are diluted with from 12 to 15 parts of water, they render it turbid, without impairing its viscid consistence; when much diluted, this consistence disappears, the liquor becomes transparent, and there separates from it a fibrous-like matter. These phenomena are, in particular, produced by the action of acetic acid. The liquor remaining after this precipitation being heated, affords albuminous pellicles, and when these are withdrawn, it gives, on evaporation, crystals of muriate and of acetate of soda. From 288 parts of synovia, there were separated by the action of acetic acid, 34 of the fibrous-like matter, and afterwards, by heat and evaporation, 13 of albumen, 5 of muriate of soda, and 3 of acetate of soda.

The fibrous matter thrown down in these experiments, is not perfectly similar to any known animal principle; for although it has some resemblance to albumen and to fibrin, it differs from both. Margueron observes, that it resembles fibrin, or rather the gluten of wheat, in colour, taste, and odour, in elasticity and tenacity; but it differs in being soluble by agitation in cold water, and being precipitated in flakes by acids and alkohol.

Alkohol separates albumen from the synovia, but not the peculiar fibrous matter, and hence the viscidity is not impaired; but it immediately disappears on adding acetic acid, and a portion of fibrous matter is deposited.

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[*] Annales de Chimie, tom. xiv. p. 125.

Synovia affords precipitates with the solutions of barytes, strontites, lime, potash, and ammonia, consisting principally of the phosphate of lime it contains; it also gives a precipitate with oxalic acid. The alkalis render it more fluid, and even dissolve it when it has been inspissated from exposure to the air.

In a moist atmosphere, it passes into putrefaction, and exhales ammonia. Decomposed by heat, it affords empyreumatic oil and carbonate of ammonia; and the residuum contains muriate and carbonate of soda. Phosphate of lime is obtained from the incineration of its charcoal.

Margueron concludes, as the result of his analysis of this fluid, that it is composed of fibrous matter 11.8, albumen 4.5, muriate of soda 1.75, carbonate of soda 7, phosphate of lime 7, the remaining quantity to make up 100 parts being water.

ARTHRITIC CONCRETIONS, which are deposited sometimes during a paroxysm of gout, in the joints, are probably formed from this fluid, or are deposited by its medium. They were found by Dr Wollaston to consist of urate of soda [*]; a discovery confirmed by the experiments of Fourcroy [†]. The connection of gout with gravel has always been observed; and the deposition of these concretions probably depends on some cause similar to that on which the formation of urinary calculi depends.

SECT. X.—OF THE AMNIOTIC FLUID.

THE fluid with which the fœtus is surrounded in the amnios, is entitled to notice, principally as having furnished what Vauquelin regarded as a new acid. He obtained it from the amniotic liquor of the cow: this has a reddish colour, an acid and bitter taste, and a faint odour. It reddens the more delicate vegetable colours. When evaporated, it is covered with a scum, in which are formed small brilliant crystals; by farther evaporation, it is reduced to the consistence of honey. If alkohol be boiled on this, a thick dark-coloured matter remains undissolved; the alkohol poured off, deposites, on cooling, brilliant crystals, in the form of slender prisms, nearly an inch long. These are the amniotic acid. They may also be obtained by reducing the liquor to one-fourth of its volume by evaporation, and abstracting a little animal matter by washing with water, dissolving, and again crystallizing them.

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[*] Philosophical Transactions, 1797, p. 589.

[†] Annales du Museum National, tom. i. p. 100.

Amniotic acid, discovered by Vauquelin and Buniva *, is white and brilliant; has a slightly sour taste, reddens infusion of litmus, is sparingly soluble in cold water, is more soluble in warm water, and crystallizes on cooling: it is also soluble in alkohol. It combines with the alkalis, and forms soluble salts, which are decomposed by the other acids, the amniotic acid being precipitated. It does not decompose the alkaline carbonates, unless when aided by heat; neither does it precipitate the earthy salts, or the nitrates of silver, quicksilver, or lead. Exposed to heat, it is decomposed, exhales ammonia and prussic acid, and leaves a bulky charcoal. In these properties it has some points of resemblance both to saccho-lactic and to uric acid; but the former differs from it in being soluble in alkohol, and in affording neither ammonia nor prussic acid, when decomposed by heat; and the latter, in its insolubility in alkohol, its different crystallization, and the red colour it receives from nitric acid.

The animal matter which exists along with this acid in the liquor of the amnios of the cow, is of a reddish brown

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* Annales de Chimie, tom. xxxiv. p. 265.

colour, a saline taste, and has a strong smell: is soluble in water; and insoluble in alkohol. Decomposed by heat, it affords prussic acid: and its charcoal, when incinerated, gives phosphate of magnesia. Nitric acid disengages from it nitrogen and carbonic acid gases, without converting it into any acid. The fluid also contains a portion of sulphate of soda, which may be obtained by crystallization.

It is singular, that the human amniotic fluid is altogether different in its composition. Vauquelin and Buniva could not discover in it any amniotic acid, but found it to consist of albumen, with a little muriate and carbonate of soda and phosphate of lime. It is of a mild saline taste, a whitish colour, and a little viscid. It becomes more milky when heated; acids render it clear. Alkohol and the alkalis separate albuminous flakes from it. Infusion of galls produces a copious precipitate; and a white precipitate is formed by nitrate of silver, from the presence of muriatic acid. According to Mr Brande, when it is procured pure, it is almost perfectly transparent, but becomes turbid on exposure to the air. It renders the tincture of violets green. Albumen separates in flakes from it when it is heated. Acids render it turbid. Alkalis added in excess, cause an evolution of ammonia *.

SECT. XI.—OF THE HUMOURS OF THE EYE.

THE ball of the eye contains three liquids differing in physical properties, though but little in chemical nature: the Aqueous Humour, situated in the anterior chamber: the Crystalline Humour, occupying the central space; and the Vitreous Humour, which fills up the greater part be-

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* Philosophical Transactions, 1809.

hind the lens. Their analysis was executed by Chenevix; from whose dissertation *, with one or two facts from a memoir by Nicholas †, the following account is taken.

Aqueous Humour. This is a clear transparent liquid, of the specific gravity of 10090, at 60° of Fahrenheit. When fresh, it has little smell, or taste. It occasions very little alteration in the vegetable colours; a little ammonia, which causes it to give a green tinge, being apparently produced from decomposition. When exposed to the air, at a moderate warmth, it evaporates, and becomes slightly putrid. When made to boil, a very small portion of coagulum is formed. Evaporated to dryness, it leaves a matter weighing not more than 8 *per cent.* of the original liquor. Tannin causes a precipitate in it both before and after it has been boiled. Nitrate of silver causes a precipitate, which is muriate of silver. No other metallic salts alter it. From these and other experiments it appears, that the aqueous humour is composed of water, albumen, and a muriate, the basis of which is soda. Nicholas discovered in it a little phosphate of lime. Berzelius gives the following as its composition,—water 98.10, albumen a trace, muriates and lactates 1.15, soda with animal matter 0.75.

Vitreous Humour. This being pressed through a rag, to free it from its capsules, Chenevix could not discover any difference between it and the aqueous humour, either in its specific gravity, or in its chemical nature. Berzelius states its composition as follows,—water 98.4, albumen 0.16, muriates and lactates 1.42, soda with animal matter 0.02.

Crystalline Humour. This differs materially from the others. It is solid and composed of concentric lamellæ; and these have a different degree of density towards the centre from what they have in the external part, the density decreasing gradually towards the circumference. The mean specific gravity is 1.100. When fresh, it is neither acid nor alkaline. It putrefies rapidly. It is nearly soluble in cold water, but is partly coagulated by heat. Tannin gives an abundant precipitate; but no traces of muriatic acid could be perceived when it was obtained free from the other humours. It is composed, therefore, of less water than the others, but of a larger proportion of albumen. Nicholas found in it also a little phosphate of lime. Its composition given by Berzelius is, water 58, peculiar matter, which he considers as similar to the colouring matter of the blood, except in colour, and which appears to be albumen 35.9, muriates, lactates, and animal matter 2.4, animal matter with some phosphates 1.3, cellular membrane 2.4.

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* Philosophical Transactions, 1803.

† Annales de Chimie, tom. liii.

These experiments by Mr Chenevix were made on the humours of the eye of sheep; but, in repeating them on those of the human eye, and of the eye of oxen, he did not find any important chemical difference. There was only a difference in the proportion of the specific gravity of the humours to each other.

SECT. XII.—OF MEMBRANE, CELLULAR FIBRE, AND SKIN.

The soft solids, enumerated under this section, have a close analogy in their properties, and appear to be the same matter under very slight modifications, having for their basis the principle denominated GELATIN.

This principle was supposed to exist in the serum of blood; an opinion which, it has been remarked, is very doubtful. It exists in some of the other animal fluids, and in several of the solids. It is from its presence that the decoctions of animal matter, when of a certain strength, become gelatinous. The skin, membranes, and white solids in general, are principally composed of it; and when the oily matter has been separated, afford it by decoction nearly pure: Glue, which is used in the arts, on account of its adhesive property, and is prepared by boiling these substances strongly in water, is solid gelatin; and isinglass, prepared from the membranous parts of the sturgeon, is the same principle in a pure form. Berzelius has affirmed, that the gelatin is a product of the operation, formed by the action of boiling water on skin or membrane, and that it does not even exist as a distinct principle in the animal frame. This seems little else than a verbal distinction: any change produced besides that of solution, must, if any, be extremely slight, and the characteristic quality of combining with tannin, seems to belong to the solid matter of these substances as well as to their gelatinous solutions. Solid gelatin, too, can be procured from bone, by abstracting the earthy matter by an acid, which is soluble in water, and gelatinous without boiling.

The property peculiarly distinguishing gelatin is solubility in water cold or warm, and giving to the water a gelatinous consistence. The proportion necessary for this is less than one part of gelatin to 150 of water. Even when the consistence is most firm, the whole becomes liquid when heated, and again gelatinates as it cools.

Alkohol precipitates gelatin; but on heating the mixture, the gelatin is re-dissolved.

The acids dissolve gelatin, and, at the same time, decompose it. Nitric acid disengages a portion of nitrogen, less considerable, however, than what is yielded by other animal substances from the same treatment: oxalic acid is formed, with a little oily matter. Sulphuric acid chars it.

The alkalis dissolve gelatin. The solutions of barytes, lime, and strontites, produce in its solution a milkiness, owing, according to Fourcroy, to the precipitation of a phosphate. Some of the metallic oxides communicate oxygen to it; and a number of the metallic salts cause precipitates to fall from its solution.

The most delicate test of gelatin is tannin. One part dissolved in 5000 of water was found by Dr Bostock to be discovered by the turbid appearance produced by the infusion of tannin. It is necessary to attend to the circumstance, that tannin likewise produces a precipitate with albumen. This, however, is much less evident; and the distinction between them is easily established by other tests. Thus, a solution of corrosive muriate of mercury, or of that form of acetate of lead known by the name of Goulard's Extract, does not affect gelatin, but renders the solution of albumen turbid.

Gelatin is very susceptible of spontaneous decomposition, and passes more quickly into putrefaction than any other variety of animal matter. Decomposed by heat, it affords carburetted hydrogen and carbonic acid, carbonate of ammonia, and empyreumatic oil; the residual charcoal contains phosphate of lime. The proportions of its elements, according to the estimate of Gay Lussac and Thenard, are given in the table in the preceding chapter.

After this general account of the properties of this principle, the history of the substances enumerated under this section, and principally composed of it, is to be given.

The Skin, which forms the external covering of the animal body, consists of two parts capable of being separated, and possessed of different chemical characters; the external thin covering named the Cuticle or Epidermis; and beneath this, a thicker and firmer layer, the Cutis or True skin. Between these, has also been described by anatomists a cellular texture, soft and gelatinous.

The first of them, the Cuticle, is nearly inorganic. When separated from the other parts, which it may be in the living animal, by the application of a blister, or when the skin has been detached by maceration in hot water, it appears extremely thin and transparent. It is softened, but is not dissolved in water, even by long boiling, a property in which it differs from the true skin, which may be dissolved. It is equally insoluble in alkohol. Solutions of the alkalis dissolve it easily, forming a kind of soap; a mutual action, which we perceive well exemplified between these substances, in rubbing a little of an alkaline ley between the fingers, the soapy feel being strong. Lime acts on it as a solvent; hence the advantage of lime in the operation of tanning; it removes the epidermis, and allows the true skin to be penetrated with the tanning liquor from each surface. The acids decompose it: sulphuric acid forms with it a kind of soapy pulp, and chars it: nitric acid stains it yellow. Hatchet considered the epidermis as principally indurated albumen, and this is confirmed by Dr John *.

The true skin, or CUTIS, is thicker than the epidermis, and consists of layers interlaced: it has considerable firmness and elasticity. When macerated in water, it swells and softens, and the blood and other animal fluids contained in it are dissolved. If boiled strongly in water, it is dissolved, and this solution presents all the characters of gelatin: it is precipitated by tannin, and by nitro-muriate of tin; and, when evaporated, forms a jelly or glue. Seguin, in his researches on the art of tanning, observed, that the skin in its dense state does not easily combine with tannin; he regarded it, therefore, as gelatin hardened by a slight degree of oxidation. Mr Hatchet has observed also the difference between skin and pure gelatin, and the differences in the skin of different animals, in the jelly or glue they afford by boiling with water. All the varieties appear to be essentially gelatin; but they differ in the degree of consistence which they communicate to water, and in the facility with which they are acted on by tannin, nitro-muriate of tin, nitric acid, and other re-agents; those

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* Annals of Philosophy, vol. vii. p. 421.

which are least consistent and viscid being dissolved, and acted on with most facility *. The most flexible skins afford gelatin more easily, and of a less viscid quality, than those which are less flexible. In the arts, the different kinds of size and glue are prepared from the skins of different animals, the skin being well cleaned, boiled in water until it is dissolved, and the decoction evaporated to the due consistence. Carpenter's glue is made from the parings of hides or horns. Size, which is a softer glue, is prepared from the clippings of parchment, glove-leather, and other finer kinds of skin.

The art of tanning skin, from the operation of tannin on its gelatin, has already (page 230.) been described.

Acids act on skin, and decompose it. The nitric acid causes an evolution of nitrogen gas or prussic acid, and a formation of oxalic acid; the skin, or the glue formed from it, dissolves, and the liquor acquires a yellow colour, which becomes deeper when it is saturated with ammonia. Muriatic acid dissolves the glue formed from skin, and the solution suffers no change for many months.

Skin is also soluble in alkaline solutions. The glues formed from it, consisting of pure gelatin, are also dissolved.

Skin in its moist state is liable to putrefaction; less so, however, the more dense and firm it is; this is even the case in a state of solution, a solution of glue being longer in showing signs of putrefaction than a solution of tremulous animal mucilage.

Skin is decomposed by heat, and affords the usual products of animal matter.

The Cellular Fibre, or net-work, the Rete mucosum of anatomists, interposed between the cutis and cuticle, has been little examined, and indeed cannot be detached from the other parts. It is the seat of the colour of the surface; and this colouring matter can be acted on through

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* Philosophical Transactions, 1800, p. 367. 368.

the cuticle, the skin of the negro being whitened by the action of oxymuriatic acid, as Dr Beddoes ascertained, though the black colour is resumed in a short time.

The MEMBRANES, which compose so large a portion of the soft solids, forming the cellular texture, the coats of the vessels, and the covering of the viscera, appear to be of the same nature. They have similar flexibility, and they dissolve more or less completely in water, forming gelatinous solutions.

SECT. XIII.—OF MUSCULAR FIBRE.

THE Muscles, or, in common language, the Flesh of Animals, present a fibrous texture; and their basis, from which they derive this, is evidently Fibrin. They consist almost entirely of this principle, with small quantities of fat, albumen, gelatin, and saline matter; derived partly at least, and perhaps entirely, from the blood, cellular fibre, nerve and fat, which are attached to it, or diffused through it.

The muscles, in the different orders of animals, are of the colour of the blood, and indeed derive their colour from it; hence, when washed with water, the colour is removed, and a white substance remains, which has all the properties of fibrin.

The water which has been employed in this operation is found, besides the colouring matter derived from the blood, to contain albumen, gelatin, saline matter, and fat, the last probably being adventitious, the other perhaps being constituent parts of the flesh. By heating this water gradually, the albumen coagulates and separates in flakes; if these be removed, and the liquor farther evaporated, it becomes gelatinous when cold; the fat, during the boiling, collects on the surface. By this simple analysis made by

Thouvenel, the immediate principles of muscle are discovered.

Besides these, he obtained a peculiar extractive matter, by evaporating the jelly to dryness, and treating it with alkohol: the gelatin and saline matter remain undissolved, and the alkohol takes up this peculiar matter, which, by evaporation, may be obtained in the solid form. It is of a brownish red colour, has a pungent, even acrid taste, and an odour somewhat aromatic: by being heated a little more than is necessary to dry it, it boils and swells, and assumes the odour and saccharine taste of caramel. It is deliquescent, and, when in solution, becomes sour from exposure to the air, passing into acetic acid, and depositing charcoal. Subjected to destructive distillation, it gives water, ammonia, and acetic acid; and its residual charcoal contains muriates of potash and soda.

By boiling water on the muscular fibre, previously washed, the saline matter it contains is dissolved. Phosphates of soda and ammonia were known to exist in the solution; and, from Hatchet's experiments, it appears, that phosphate and carbonate of lime are also present. They are more abundant in the muscle of beef than in that of veal; and hence it is probable, as this chemist remarks, that the earthy matter is more abundant in the coarse and rigid fibre of adult and aged animals, than in the tender fibre of those which are young. In young animals, the gelatin is more abundant in the muscular fibre than in those of advanced age; in the latter, the fibrin appears to predominate.

When the entire flesh is boiled in water, its principles are more completely dissolved, except the fibrin, which is in part dissolved, but which partly also forms threads that float in the liquor. The gelatin and albumen are detected in the liquor by the infusion of tannin. Lime-water, or ammonia, produces in it a slight precipitate of phosphate of lime: oxalic acid detects lime; and, according to

Fourcroy, nitrate of silver indicates the presence of muriatic acid. If the decoction be strained and evaporated, it becomes gelatinous; and by being boiled sufficiently, it becomes solid and firm, and can then be preserved for a long time without injury. Compositions of this kind, with the addition of aromatics and a little salt, form the tablets of portable soup.

When flesh is exposed to the air, it soon becomes tainted, and at length putrid,—a change which, as Mr Hatchet has supposed, depends principally on the presence of gelatin; as he found, that when deprived of this principle by maceration and subsequent boiling, it is little liable to this change. Berthollet found, that if the gelatin be removed by boiling, so that the liquid gives no precipitate with tannin, on exposing the flesh to the air for some days, oxygen is consumed and carbonic acid formed; a putrid odour is acquired; and there is a formation of gelatin, so that the water boiled on the flesh gives a copious precipitate with tannin. These results can be obtained a number of times, though to a less extent, and at length the flesh is converted into a substance resembling cheese *.

When the air is excluded, and the flesh is immersed under water, it suffers a peculiar species of decomposition, in consequence of which it is converted into a fatty matter like spermaceti,—a change which is to be considered under the history of the general chemical changes to which animal matter is liable.

Exposed to heat, flesh affords the usual products of the decomposition of animal matter. Berthollet, examining the acid which it yields, supposed it to be of a peculiar nature: he named it the Zoonic; but it has since been discovered to be the acetic. Five hundred grains of the washed muscular fibre of beef, left, in Mr Hatchet's experiments, 108 grains of charcoal, which, by incineration, afforded

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* Mémoires de la Société d'Arcueil, tom. i. p. 555.

25.6 grains of earthy residuum, the greater part of which was carbonate of lime, with a small proportion of phosphate, and a little pure lime.

The acids decompose the muscular fibre, with results nearly the same as those produced by their action on fibrin. The action of nitric acid is, in particular, important. Berthollet long ago remarked, that it caused an evolution of nitrogen gas. Mr Hatchet found, that washed muscular fibre, acted on by nitric acid diluted with three parts of water in the cold, is converted into a substance soluble in boiling water, and analogous to gelatin; the acid acquires a yellow tinge; and the residual matter consists principally of fat, with undecomposed muscular fibre. When the washed flesh is acted on by boiling nitric acid, it is dissolved; the solution is of a yellow colour, and a portion of fatty matter floats on the surface: ammonia throws down a precipitate of oxalate, with a little phosphate of lime. When the recent muscle, without any preparation, is dissolved in nitric acid, the solution, when saturated with ammonia, becomes of a deep orange colour, and forms animal soap with the alkalis *.

The action of nitric acid on the muscular fibre was investigated more minutely by Fourcroy and Vauquelin †. The gas given out when heat was applied, the acid being diluted with an equal quantity of water, they found to consist of nine-tenths nitrogen and one-tenth carbonic acid. The residuum consisted of the remains of the flesh, retaining in part its fibrous appearance, of a yellow colour, and of a yellow fatty matter, collected on the surface of the liquor. The residual fibrous matter gave to boiling water a yellow colour, and the property of reddening vegetable blues; and even after having been repeatedly washed, it continued to give colour, though no longer acidity.

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* Philosophical Transactions, 1800, p. 391. 393.

† Annales de Chimie, tom. lvi. Nicholson's Journal, vol. xiii.

Its solution in alkalis is of a blood-red colour: acids precipitate it in yellow flakes. It feels greasy and pitchy; has a rancid smell, and a bitter taste; and melts, swells, and gives an oily vapour when heated. It was found to saturate alkalis, so as nearly to disguise their properties. The yellow matter even decomposes the alkaline carbonates in the cold with effervescence, and likewise the solution of acetate of potash, with the assistance of a gentle heat. By the application of alkohol, this substance was found to consist of a small quantity of unctuous matter, which the alkohol takes up, and of an acid, which, from its colour, these chemists named Yellow Acid. This acid, when freed from the fat which disguises its properties, is of a deeper colour, reddens more strongly the vegetable colours; it no longer melts, and does not exhale the odour of burnt grease, but fœtid and ammoniacal vapours. It combines with ammonia, which it deprives of its odour. Dissolved in fat, it communicates to it acidity and rancidness. Subjected to destructive distillation, it gives the usual products of the decomposition of animal matter.

The acid liquor obtained in the process had a yellow colour: when saturated with carbonate of potash, its colour changed to orange: afterwards it became turbid, and deposited a small quantity of orange-red powder. There is thus obtained a small portion of the detonating matter which is formed in the action of nitric acid on indigo. By distillation, a colourless liquor, of a rancid taste, containing a little ammonia, was obtained. On distilling the liquor, without the previous addition of carbonate of potash, a similar colourless fluid passed over: what remained in the retort had become yellow by concentration: when concentrated, crystals formed in the midst of a liquor, viscid, and having an acrid bitter taste: on the addition of a little potash, it became of a blood-red colour: mixed with alkohol, it gave a precipitate, consisting of a mixture of sulphate of lime and super-oxalate of potash.

It gave a second precipitate with lime-water, consisting of oxalate of lime. After this double operation of alkohol and lime-water on this concentrated liquor, on being evaporated farther, it was converted into a brown viscid syrup, of a bitter taste; which being again mixed with alkohol, threw down a copious precipitate of malate of lime, the alkohol retaining dissolved a portion of yellow acrid matter.

There are thus formed, through the whole of this operation, 1*st*, A yellow insipid matter, of little solubility, though acid, and which immediately succeeds the fleshy fibre. 2*dly*, Another yellow matter, bitter, more soluble, and equally acid, which remains dissolved in the nitric liquor. 3*dly*, An inflammable detonating substance, which is also retained in solution; and, *lastly*, Oxalic and malic acid. It is the opinion of Fourcroy and Vauquelin, that the yellow and nearly insoluble matter is the first degree of change produced upon the muscular fibre: it passes quickly to the second degree of alteration and of acidity, whose product is the more soluble yellow matter; this, by a third degree of alteration, is succeeded by the inflammable detonating substance, being the third and last term of the decomposing action of nitric acid. They attribute the successive formation of these compounds to the subtraction of part of the azote, and of a more considerable portion of the hydrogen: by this means there remains an excess of carbon and of oxygen, which produces the state of fat and acidity already noticed. They examined if the acidity of the yellow substances arose from nitric acid; but after a careful investigation, they were satisfied that it was not present. The formation of oxalic and malic acids they considered as belonging to the white mucous scales of the cellular membrane, from finding, by comparative experiments on the effects of nitric acid on the white membranaceous organs, that they furnished these acids, and very little of the fat yellow matter.

The yellow principle obtained in these experiments, appears to have some relation with the bile. It is accordingly stated by these chemists, that the red matter of biliary concretions, when separated from the bitter green matter with which it is combined, displays similar properties with the yellow fibrous matter. A substance similar to it, too, was obtained from the urine of a person labouring under jaundice, by evaporating it, and treating it with alkohol. They suppose even, that it is it which gives the yellow colour to bile.

This yellow acid and bitter matter appear to be analogous to the amer and yellow acid formed by the action of nitric acid on indigo, already noticed under the history of indigo. According to Thenard and Chevreul, they are compounds of animal matter with nitric acid; and the combination is so intimate, that the acid is not abstracted by potash; but is discovered only when the compound is decomposed by heat *. Berzelius, as has been already stated under the history of the blood, considers the two yellow products as compounds of fibrin and nitric acid; the insoluble one having an excess of acid, the soluble being neutral.

SECT. XIV.—OF TENDON, LIGAMENT, CARTILAGE, HORN, HAIR, &C.

THESE substances differ from those described in the preceding sections, in their greater firmness and hardness; and they form a gradation into those which are still more highly indurated, bone and shell. The chemical constitution of some of them has been only imperfectly investi-

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* Mémoires d'Arcueil, tom ii. p. 491.

gated. Ligament, tendon, and muscle, it is observed by Mr Hatchet, seem to glide almost imperceptibly into each other: they are connected with cartilage, as it is, on the other hand, with horn; and the basis of all of them appears, from the experiments of this chemist, to be albumen. I have therefore placed them under one section.

The TENDONS, which are cords or flat sheaths connecting the muscles with the bones, have a great degree of toughness and elasticity: their texture is fibrous. They are with difficulty acted on by water. It has been stated, that by long boiling they are dissolved, and their solutions form a jelly or glue: they may afford so much gelatin as to form a gelatinous fluid, but it is doubtful if they are entirely soluble.

The LIGAMENTS connect and bind the bones together at their articulations: they are fibrous in their texture, the fibres running longitudinally; are possessed of great strength and cohesion; can be stretched out, have a degree of elasticity, and are not easily broken. When boiled in water, they afford a portion of gelatin, the water being rendered turbid by infusion of tannin; but the entire substance cannot be dissolved, and it even often remains, after the boiling, with its texture little altered. Its basis, therefore, is not gelatin, but appears rather to be indurated albumen.

CARTILAGE forms the transition to bone: it has so much induration, as to require some exertion of force to bend it; and in a morbid state, is often so highly indurated as to be ossified. Bone, on the other hand, is in the first stages of its formation and growth cartilaginous; it sometimes becomes so, too, from disease: and a cartilaginous matter exists in the hardest bones, and forms their basis, from which the other ingredients, the gelatin and earthy matter, may be removed by their solvents.

Cartilages are solid, but soft and easily cut; highly clastic, dense in their texture, white and semi-transparent. They cover the articulated extremities of bones, or sometimes form distinct parts.

The chemical properties of cartilage are not very well determined, and appear to vary in different cartilages. Thus Mr Hatchet has remarked, that the cartilages of the articulations are completely soluble when long boiled with water; but this does not happen when other cartilages are thus treated *. They are, however, softened by maceration in water, and by long boiling are nearly entirely dissolved.

The little action exerted even by the more powerful chemical re-agents on cartilage, is shewn by the fact, that in subjecting bone to the action of diluted muriatic or nitric acid, though the gelatin and the phosphate of lime are dissolved, the cartilaginous part remains undissolved, transparent, and presenting the figure of the bone. The concentrated acids erode or dissolve it.

As the matter of cartilage thus differs from gelatin, and as it is comparatively insoluble and inactive, it is probably, as Mr Hatchet supposed, indurated albumen. The same matter he considers as the essential part of horn, hair, feather, quill, hoof, nail, and shell, varying only in its consistency from a soft jelly to an elastic, brittle, and hard body like tortoise shell, but in all these of similar chemical properties. From experiments on these bodies, which did not give any essential difference in the results, it appears, that this matter is softened when boiled in water, and the water becomes slightly turbid with nitro-muriate of tin, but suffers no change from the tanning principle. Muriatic and sulphuric acids have little effect on it unless heated. The same is the case with nitric acid much diluted, or in the state proper to extract and separate gelatin; but if the immersion in the dilute acid be continued during some weeks,

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* Philosophical Transactions, 1810, p. 370.

the acid acquires a yellow tinge, and, when saturated with ammonia, becomes of a deeper colour without having its transparency impaired. The substance macerated is softened and becomes more transparent: if immediately immersed in pure ammonia, its colour changes to a deep orange, inclining to blood red, and it is gradually dissolved; if washed in distilled water and boiled, it is dissolved, and forms a liquor, precipitated like gelatin by infusion of tannin and nitro-muriate of tin. If the nitric acid is not sufficiently diluted, or if heat be applied, the whole is rapidly dissolved with effervescence. The fixed alkalis combine with this principle in all its varieties, and form saponaceous compounds, ammonia being disengaged during the combination, and charcoal precipitated. Decomposed by heat it gives a small portion of water, some carbonate of ammonia, a fœtid empyreumatic oil, carburetted hydrogen, and carbonic acid gases and prussic acid. Its coal affords little saline matter, principally phosphates.

Mr Hatchet, from some comparative experiments on pure coagulated albumen dried, obtained results almost precisely the same. There can be therefore little doubt, that albumen is the basis of the substances above described, existing in them, with variable proportions of gelatin, and sometimes with phosphate and carbonate of lime. These earthy salts he considers as not essential to the constitution of cartilage, but when present, as extraneous or foreign to the composition *.

The chemical nature of HORN is similar to that of cartilage; and with regard to physical qualities, it differs little except in its greater induration. It is hard, so as not to be easily bent, unless when artificially softened, but it can be easily pared or cut; its texture is close and smooth, and it is more or less transparent. When heated, it is softened, and is then capable of being moulded into any form.

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* Philosophical Transactions, 1799.

Shavings of the horns of different animals, when boiled a long time in water, were found by Mr Hatchet to afford small quantities of gelatin: the most flexible horns yielded the largest quantity, and most easily; and when deprived of it, and allowed to dry spontaneously, they became more rigid and more easily broken: this residual matter Mr Hatchet regarded as indurated albumen, a conclusion confirmed by John. He found farther, that they yield a quantity of phosphate of lime, so small that it can scarcely be regarded as an essential ingredient.

These observations apply to the horns of the ox, ram, goat, and chamois; it is singular, that the stag's or buck's horn is of a very different nature, as is evident from the products it has been long known to afford when decomposed by heat, which are analogous to those of bone. Mr Hatchet has accordingly remarked, that like bone it affords much phosphate of lime and gelatin.

Hoof appears to be not only of a mechanical structure, but likewise of a chemical composition similar to horn; the shavings of ox's hoof, when long digested in water, affording, as Mr Hatchet found, a liquor which is only made slightly turbid by nitro-muriate of tin.

The matter of the Nail is in like manner softened by digesting in boiling water for several days, and affords a slight cloud on the addition of nitro-muriate of tin. It too consists of indurated albumen.

Similar results were afforded by the horny scales of serpents and lizards, as well as of certain insects, and by tortoise shell; and there can be little doubt that these are of the same chemical composition as horn.

Feather and Quill, chemically considered, appear to be similar to these, and to have the same basis of indurated albumen. Digested in boiling water, they did not afford any trace of gelatin by the test of the tanning principle, but nitro-muriate of tin produced a faint cloud.

Even Hair, though apparently remote from these substances in mechanical structure, appears to be the same, or nearly so, in chemical composition. Mr Hatchet found, that when it was long digested with distilled water, it imparted a small portion of gelatin, which was precipitated by tannin, and by nitro-muriate of tin; and when the hair after this was dried in the air, its flexibility and elasticity were much diminished; it was also little liable to farther spontaneous change, and had all the characters of indurated albumen. Vauquelin submitted hair to a more minute examination. He found, that though insoluble in water boiling under a common pressure, it may be dissolved in Papin's digester, when the temperature is higher. If the temperature was raised high, the hair even suffered decomposition, carbonate of ammonia, empyreumatic oil, and sulphuretted hydrogen being evolved. When the solution of hair is thus effected, an oily matter is separated, and the liquor gives copious precipitates with infusion of galls and with oxymuriatic acid. It is also rendered turbid by the other acids, but an excess of acidity restores its transparency. It does not gelatinize, even when much concentrated by evaporation. A dilute solution of potash dissolves it, hydro-sulphuret of ammonia being evolved, while a little oil, sulphur, and iron, remain undissolved. The acids gradually dissolve and decompose it, nearly with the same results as are given by analogous animal substances. Alkohol digested on hair, extracts a portion of oil, or rather two oily fluids differing in colour, and differing according to the colour of the hair itself. From black hair, there first separates, as the alkohol cools, an oily matter in white scales; and, on evaporating the alkohol, a concrete dark-coloured oil: from red hair there are obtained, first a white, and afterwards red oil: the colour of the hair seems to reside in this oily matter, and also, as Vauquelin supposes, in the darker coloured hair, on sulphuretted iron; this colour is destroyed by oxymuriatic acid gas. He found hair, on incineration, to afford phosphate, sulphate, and carbonate of lime, muriate of soda, silex, magnesia, and oxides of iron and manganese, the whole amounting to a very small proportion of the hair, and varying in hair of different colours *.

The structure of hair appears close, and its surface, even when viewed with the microscope, smooth. Yet, as Monge has observed, it is certain that it is not equally smooth when rubbed in different longitudinal directions, but is composed either of scales like those of fish, or imbricated zones like the horns of animals; hence its tendency to be entangled: on the same property is founded the art of felting hair, subservient to that of hat making. The details of this art are stated by Chaussier †, and in a memoir by Mr Nicholson ‡.

Wool is a finer kind of hair. It has one characteristic property of what Mr Hatchet regards as indurated albumen, that of forming a soap with alkalis, and this in so high a degree, that it was proposed by Chaptal to be employed as a substitute for oil or fat in the manufacture of soap; woollen rags or clippings of wool being boiled in an alkaline ley to saturation: the product is a soft soap of a grey colour, soluble in water, and possessed of sufficient detersive power ||. It has not been established in use, partly as it gives a grey colour to the thread or cloth, and hence could not be applied to linen, and partly from its disagreeable smell, which is only imperfectly removed by exposure to the air. It is not improbable, that it might be used with advantage in cleansing wool previous to dyeing; and from the observations of Chaptal, it is probable that it may act as a mordant.

From the experiments of Berthollet it appears, that wool

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* Nicholson's Journal, vol. xv. p. 141.

† Ibid. 4to, vol. i. p. 399.

‡ Ibid. vol. iii. p. 23. 73.

|| Ibid. vol. i. p. 40.

acted on by nitric acid affords oxalic acid and a fatty matter; the same products, with a less proportion of the former, being afforded by hair. He found too, that wool is dissolved by sulphuric and muriatic acids, ammonia being formed, and charcoal deposited.

With the substances, the chemical history of which has now been given, may lastly be associated SILK, as connected with them in properties and chemical relations. The fibres of silk are spun by the caterpillar of a species of phalena, the Phalena Bombyx, a native of China; the silk worms, however, have been naturalized in several countries. The silk is inclosed in two small bags, in very fine fibres of different shades of colour, from a white to a faint yellow or red, shining from a varnish with which it is naturally covered, and from which it derives stiffness and elasticity: this varnish is soluble in water, but not in alkohol; and its watery solution gives a precipitate with tannin. The colouring matter appears not to be essential to silk; it is soluble in alkohol, and approaches in its properties to a resin. To adapt it to use, silk is freed from these substances, principally by the action of weak alkaline leys, soap, alkohol, and diluted acids, and especially the muriatic acid diluted with alkohol according to the process for bleaching silk, discovered by Beaumé *.

Silk is not soluble in water, even at a boiling heat: it is equally insoluble in alkohol. The alkaline leys dissolve and decompose it, ammonia being evolved. The acids erode and dissolve it. Nitric acid renders it yellow, disengages nitrogen gas, forms prussic acid, and, according to Berthollet, oxalic acid, with a portion of fatty matter. This action was examined by Welter †; he discovered, that, by the repeated distillation of nitric acid from silk, a peculiar matter, which he named Bitter Principle, is

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* Nicholson's Journal, 4to, vol. i. p. 52.

† Annales de Chimie, tom. xxix. p. 301.

formed : it is of a golden yellow colour, soluble in water and in alkohol, capable of crystallizing on cooling, inflammable, and having a very bitter taste ; it appears to be the same substance as the yellow bitter acid already noticed, as formed by the action of nitric acid on the muscular fibre.

Silk is decomposed by heat, and affords the usual products of animal matter. The proportion of carbonate of ammonia is very large.

The silk-worm forms an acid liquor, which was imperfectly examined by Chaussier. On the supposition that it was a particular acid, it received in the new nomenclature the name of Bombic Acid ; but there is reason to believe that it and some other acids formed by insects, are acetic acid slightly disguised. That secreted by the ant, and named Formic Acid, had been considered as a peculiar acid by Margraaf and Arvidson, who examined its properties ; but Fourcroy and Vauquelin affirmed it to be a mixture of acetic with phosphoric acid, and a little animal matter *. Gahlen has since examined it, procuring it by first super-saturating the acid liquor from the ant by carbonate of potash ; decomposing and distilling by means of sulphuric acid ; combining the distilled acid with oxide of copper, and again decomposing this formiate by sulphuric acid. This distilled acid had a peculiar taste and odour, with a greater specific gravity than that of concentrated acetic acid. It saturated different proportions of bases from those saturated by acetic acid, and afforded different salts †. Berzelius has, from its analysis in his usual method, given as its composition, carbon 32.970, oxygen 64.223, and hydrogen 2.807 ‡. But these are the proportions as inferred from it in the state in which it exists in formiate of lead, in the formation of which there will

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* Annales du Museum d'Histoire Naturelle, tom. ix. p. 411.

† Annales de Chimie, tom. lxxxiii. p. 208.

‡ Annals of Philosophy, vol. ix. p. 107.

probably be a formation of water, the oxygen and hydrogen of which therefore require to be added to give the real composition. With this correction, the proportion of oxygen to carbon will probably be found to be that constituting carbonic acid, and the proportion of hydrogen that existing in super-carburetted hydrogen.

SECT. XV.—OF BONE AND SHELL.

THE substances to be described under this section are distinguished by the large quantity of earthy matter which enters into their composition, and communicates to them solidity, hardness, and other characters: phosphate of lime is predominant in bone, carbonate of lime in shell, though each frequently contains portions of both these, and sometimes phosphate of magnesia.

BONE, which composes the most solid part of the animal frame, giving figure to the whole, and serving as the support of motion, and the covering with which many of the organs are protected, presents some varieties of structure and of form. In general, the bones appear to be composed of laminæ in more or less perfect adhesion. Flat bones are dense towards the surface, while, in the middle or inner part, the laminæ separate, and the texture is spongy. In the long cylindrical bones, the external surface is dense; but towards the internal part the density is diminished, a spongy or cavernous structure is apparent, and there is a cavity, in which a matter of a fatty nature, the marrow, is contained; a portion of this appears even to be diffused through the more dense part of the bone. Externally, the bones are covered by a membrane, the Periosteum, and they are penetrated by blood-vessels, absorbents, and nerves.

Bone admits of a simple analysis, by which its immediate principles are discovered. When boiled in water, the decoction is found to contain a considerable portion of gelatin, and, if the boiling has been long continued, concretes into a jelly on cooling. If the bones be previously rasped, the quantity of gelatin obtained is much larger; and in this way, as Proust has shewn, bones may be economically used to prepare a nutritious article of diet *.

During the boiling of bones in water, a portion of fatty matter collects on the surface. This may be derived from the marrow diffused through the bone, and can scarcely be considered as essential to the bony matter. It is also extracted along with the gelatin by alkaline solutions.

If a piece of bone be digested in dilute muriatic or nitric acid, the gelatin and earthy matter are dissolved, and there remains a firm cartilaginous substance, presenting the figure of the bone. By this experiment cartilage, considered by Hatchet as analogous to albumen, is proved to be a constituent ingredient of bone. If the acid be much diluted, the earthy matter only is dissolved, and the gelatin and cartilage remain. This has been employed by Darcet, as an economical method of procuring the animal matter of bones for nutrition, and is preferable to the converse mode of extracting the gelatin from the earthy matter by strong boiling, as in the latter the extraction is only imperfect, and the continued heat gives an unpleasant taste. The process he employs, is to submit the bones to very dilute muriatic acid, and after the earthy matter is dissolved, to wash the residual gelatin thoroughly with cold water. It then dissolves easily in water by boiling †.

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* Nicholson's Journal, 8vo, vol. i. p. 100.

† Philosophical Magazine, vol. xlvi. p. 17. Some details with regard to both methods of extracting the nutritive matter from bones, are given on the authority of a Society of Geneva, Annals f Philosophy, vol. xi. p. 106.

From the quantity of animal matter which bone contains, it affords, when exposed to heat in close vessels, a large quantity of carbonate of ammonia, with a fœtid oil; and this process is followed on a large scale, to procure ammonia. The water which distils over, contains, according to Fourcroy, a little prussic and sebacic acids saturated with ammonia; carbonic acid, carburetted, and sulphuretted hydrogen gases, are disengaged. When heated in an open fire, the oil of the bone is melted, and burns with a fœtid odour. The bone is charred; but by continuing the application of heat, it becomes white, when there remains merely the earthy salts which it affords. This forms a porous mass, which cannot be vitrified but by a very intense heat.

If bones be calcined in an open fire, the animal matter they contain is decomposed and burnt out, and they are converted into a white earthy-like substance, retaining the figure and even the structure of the bone. This is what the chemists formerly termed the earth of bones. Gahn discovered it to be phosphate of lime. It is likewise separated during the decoction of bone in water under increased pressure, by which the temperature being more elevated, the cartilage is softened, and the gelatin completely dissolved: it is also dissolved by the action of an acid on bone. Along with this phosphate of lime are smaller portions of other earthy salts, chiefly carbonate and sulphate of lime. A little carbonate exists in the recent bone; but the greater part of it found in the burnt bone, as well as the sulphate, appear to be products of the combustion, while the phosphate of lime is evidently an essential ingredient. Fourcroy and Vauquelin found, in the bones of the ox, horse, sheep, and of birds, phosphate of magnesia, while they could not discover it in human bones; a singularity which, they observed, is probably connected with the fact, that phosphate of magnesia is contained in the urine of man, but not in that of other animals; that, therefore, this earth is discharged from the human system by this excretion, instead of being deposited in the bones. Berzelius, however, discovered a portion of it in human bone; and by a more recent investigation, the former chemists also found a small portion of magnesia in human bone. They likewise found minute portions of alumina and silica, manganese and iron *. Berzelius farther detected fluate of lime.

The minute analysis of burnt bone is effected by the agency of the acids. When the acid is added to it in powder, effervescence is excited, from the disengagement of the carbonic acid of the carbonate of lime; the gas has also a pungent smell, which has been ascribed to the presence of prussic acid, but may be owing to fluoric or sulphurous acid. If sulphuric acid has been employed in the decomposition, a large quantity of sulphate of lime is formed, and a super-phosphate of lime is produced, soluble in water, which is therefore carried off by washing,—a process which, as has been already remarked, is followed to procure that acid for the preparation of phosphorus. If, instead of sulphuric, nitric acid be employed in the analysis, the constituent parts of the burnt bone are better discovered. It is entirely dissolved; the carbonic acid of the carbonate of lime is disengaged during the solution, and may be collected: the phosphate of lime may be precipitated by the addition of pure ammonia: by adding to the residual liquor nitrate of barytes, sulphuric acid is detected; and from the quantity of precipitate, the proportion of sulphate of lime, from the decomposition of which it had originated, may be inferred. To discover the quantity of lime which had been combined with the carbonic acid disengaged during the solution, Mr Hatchet added carbonate of ammonia, and obtained a precipitate of carbonate of lime,—a method

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* Annales de Chimie, tom. lxxii. Nicholson's Journal, vol. xxx. p. 256.

not unexceptionable, since the precipitate might in part arise from the decomposition of the sulphate of lime in solution; or, where this had been decomposed by a previous addition of nitrate of barytes, from the nitrate of lime which must thus have remained in the liquor. The quantity produced, however, Mr Hatchet observes, was much greater than the quantity of sulphuric acid, indicated by the precipitation of barytes, could have saturated. The phosphate of magnesia, which Fourcroy and Vauquelin discovered in the burnt bones of the inferior animals, was detected by precipitating the liquor obtained from the mixture of burnt bones and sulphuric acid, by ammonia, adding the ammonia in excess. The precipitate consists of phosphate of lime and phosphate of magnesia and ammonia: to separate these, it was boiled in a solution of potash, which disengages the ammonia, and attracts the acid of the magnesian ammoniacal phosphate, leaving the magnesia mixed with the phosphate of lime. These are separated by boiling them in acetous acid, which dissolves the former, leaving the latter undissolved: from the solution of acetate of magnesia, the magnesia may be precipitated by carbonate of soda; and the carbonate of magnesia, if free from lime, will form a transparent solution with sulphuric acid. The quantity of phosphate of magnesia amounts to about a fortieth part of the calcined bone.

The sulphate and carbonate of lime, indicated by the analysis in calcined bone, may be products of the calcination, and not constituent parts of the bone. In the bony matter, there probably exists more lime than the phosphoric acid can saturate: carbonic and sulphuric acids will be formed during the calcination of the bone, from the decomposition of the animal matter, of which the bases of these acids are elements; and they will be attracted by the excess of lime. A portion of carbonate of lime is indeed indicated in recent bone by Mr Hatchet's experiments, a slight effervescence attending its solution in an acid; but the quantity appears to be inconsiderable, and by Merat-Guillot it is stated, in the bones of land animals, to amount to not more than 1.5 in 100 parts *.

The entire quantity of lime and of phosphoric acid contained in bones, may probably be best determined by the method pointed out by Fourcroy and Vauquelin,—precipitation of the lime by oxalic acid from the solution of calcined bone in diluted nitric acid. The liquid may be evaporated, and by a strong heat the nitric acid may be expelled, leaving the concrete phosphoric acid; or the phosphoric acid may be precipitated by acetate of lead. The minute details of the complicated analysis of bone, are given by these chemists in their memoirs on this subject †.

Bone is not much liable to spontaneous decomposition; even the animal matter suffers little change for a long period; the re-action of its elements, as well as the action of air and humidity, being prevented by the solidity communicated by the phosphate of lime: hence bones which have been buried in the earth retain a large quantity of it, as Merat-Guillot found ‡. In fossil bones, however, or those which have been long buried, and have in consequence undergone some changes, particularly from the infiltration of carbonate of lime, the animal matter appeared, from Mr Hatchet's examination, to have been completely removed; and the phosphate of lime remained intermixed with the carbonate of lime; the latter substance, by its chemical agency, probably having contributed to the decomposition of the animal matter. Vauquelin, in examining fossil bone or ivory, found in different specimens, different quantities of animal matter remaining, some losing 45 *per cent.* by calcination, others not more than 15 ||.

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* Annales de Chimie, tom. xxxiv. p. 71.

† Nicholson's Journal, vol. viii. p. 86. xxx. p. 256.

‡ Annales de Chimie, tom. xxxiv.

|| Philosophical Magazine, vol. xxv. p. 265.

The body of the teeth of animals is bone, and presents the same chemical results. It dissolves, Mr Hatchet remarks, with a feeble effervescence in dilute nitric acid, leaving its cartilaginous basis retaining the shape of the tooth. The external covering, or Enamel, is different. Mr Hunter remarked, that when immersed in an acid, it left no cartilaginous part; and Hatchet found, that when exposed to heat, it emitted little or no smoke or empyreumatic odour. Josse obtained the same results, and, when boiled in water, the decoction gave so slight a precipitate with tannin, as scarcely to indicate the presence of gelatin; neither was it softened by boiling in water under increased pressure *. It appears, therefore, to be nearly destitute of animal matter. It dissolves in acids, with a slight effervescence, as Dr Blake remarked, and Josse has confirmed, and appears therefore to consist of phosphate, with carbonate of lime.

The presence of fluoric acid combined with lime in the enamel of teeth was announced by Morichini, an Italian chemist. He observed it in the enamel or outer layer of the fossil teeth of the elephant, which he found to be composed almost entirely of fluate of lime, while the body of the teeth was composed of phosphate. On submitting the enamel of human teeth to the same trials, he found, that it contained a large proportion of fluate, vapours of fluoric acid being exhaled when the enamel was acted on by sulphuric acid. Gay Lussac so far confirmed this discovery, as to have found fluate of lime in ivory, copious vapours of fluoric acid being exhaled from it when concentrated sulphuric acid was poured upon it †. And with this the experiments of Fourcroy and Vauquelin agreed, fluate of lime appearing to exist in small quantity in fossil ivory, especially in that state in which the animal matter had

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* Nicholson's Journal, 8vo, vol. v. p. 58.

† Philosophical Magazine, vol. xxiii. p. 264.

been most completely removed *. These chemists were unable, however, to discover fluoric acid in new ivory or in the enamel; Mr Brande likewise found, that when enamel is subjected to the action of sulphuric acid aided by heat, no vapours but those of sulphurous or sulphuric acid are exhaled †. Its existence, however, in the enamel of human teeth and oxen teeth, as well as in the bones of animals, has been confirmed by Berzelius, as has been already stated.

The proportions of the principles of bone must differ in different states: in the bones of young animals, the gelatin and cartilage are in larger proportion than in more advanced age. The quantity of gelatin extracted by boiling in water is from 25 to 50 from 100 parts, and the remainder is principally phosphate of lime. The phosphate of magnesia is always in very small quantity, not exceeding 2 in 100 parts; and the fluate of lime, according to the experiments of Berzelius, is in not much larger proportion ‡. Ox-bone, according to an analysis by Fourcroy and Vauquelin, consists of gelatin 51, phosphate of lime 37.7, carbonate of lime 10, phosphate of magnesia 1.3 ||. The following are assigned by Berzelius as the proportions of the earthy ingredients in calcined human bone, phosphate of lime 81.9, fluate of lime 3, lime 10, phosphate of magnesia 1.1, soda 2, carbonic acid 2 §. He has also given the following table of the composition of bone, and the enamel of teeth ¶.

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* Philosophical Magazine, vol. xxv. p. 265.

† Nicholson's Journal, vol. xiii. p. 214.

‡ Philosophical Magazine, vol. xxviii. p. 306.

|| Nicholson's Journal, vol. viii. p. 87.

§ Annales de Chimie, tom. lxxxviii. p. 199.

¶ Journal de Physique, tom. lxiv. p. 355.

	Dried Human Bones.	Enamel of Human Teeth.	Bones of Oxen.	Enamel of Oxen Teeth.
Cartilage	32.17	—	33.30	3.56
Blood-vessels	1.13	—		
Fluate of lime	2.00	3.2	2.90	4.00
Phosphate of lime	51.04	85.3	55.45	81.00
Carbonate of lime	11.30	8.0	3.85	7.10
Phosphate of magnesia	1.16	1.5	2.05	3.00
Soda, muriate of soda, water, &c.	1.20	2.0	2.45	1.34
	100	100	100	100

A more ample table has been given by Merat-Guillot, of the composition of the bones of different animals, and some similar substances, which does not appear, however, to contain very accurate results *.

The Shells with which the bodies of many marine, and a number of land animals are covered, are analogous in their structure to bone, but they differ in chemical constitution, phosphate of lime being the basis of the one, while carbonate of lime exists in much larger quantity in the other. Mr Hatchet undertook the examination of this subject, and established the result, that shell and bone, in their different varieties, constitute two genera, in both of which animal matter is contained, in the one indurated by phosphate, in the other by carbonate of lime: And these are connected by a certain order of substances,—the crustaceous coverings of certain marine animals, and likewise some of the species of zoophytes, in which, with the animal matter, are intermixed variable proportions both of carbonate and phosphate of lime.

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* Annales de Chimie, tom. xxxiv. p. 71.

In Mr Hatchet's experiments, the shell submitted to examination was immersed in acetic acid, or nitric acid diluted with 4 or 6 parts of water. The carbonate of lime was precipitated by carbonate of ammonia or potash; and phosphate of lime (if present) was previously precipitated by pure ammonia. If any other phosphate was suspected, it was discovered by acetate of lead.

The greater number of marine shells are of two descriptions, either of a porcellaneous aspect, with an enamelled surface and fibrous texture, or they are composed of the substance called Nacre or Mother of Pearl. The first kind dissolve in the acids with strong effervescence; their solutions afforded no trace of phosphate of lime, or of any other combination of phosphoric acid: they contained only carbonate of lime; and the animal matter which acts as a cement to this, indurated albumen, is in small proportion; hence, when the shells are exposed to heat, they exhale little empyreumatic odour; they emit no smoke: and when dissolved in acids, little or no vestige of it can be discovered by any flocculent or gelatinous residuum.

In shells of the other description approaching to nacre, the earthy matter is also carbonate of lime, but it is present in smaller proportion, while the animal matter is in large quantity. Hence they give much smoke, and a strong empyreumatic odour, when exposed to heat; and when acted on by acids, give out less carbonic acid, and leave a large quantity of a membranaceous or cartilaginous residuum, retaining often the figure of the shell. This substance often constitutes a large part of the shell, as in that of the oyster or muscle, and is so much indurated as to be no longer gelatinous; it appears to be deposited in layers, each having a corresponding coat of carbonate of lime. Mother of pearl, and likewise pearls, were found to be of similar structure and composition. Their waved appearance and their iridescence, are evidently the effects of this lamellated arrangement, and of the nebulous semi-transparency of the substances composing it.

An extensive class,—the zoophytes, comprehending the varieties of madrepore, millepore, tubipore, were found to consist of carbonate of lime with animal membrane.

Mr Hatchet found, that the substance analogous to shell, which covers crustaceous marine animals, as the echini, crab, lobster, &c. is different. It had the same cementing animal matter, but with this were united both carbonate and phosphate of lime, forming therefore a substance intermediate between bone and shell. The shells of the eggs of birds were of similar composition; and even some of the zoophytes, as various species of isis, gorgonia, &c. gave indications of phosphate of lime, intermixed with the carbonate of which they are chiefly composed.

SECT. XVI.—OF FAT, STEARIN, ELAIN, MARGARIC, OLEIC, AND SEBACIC ACIDS. SPERMACETI.

FAT appears to be a secreted matter, as no traces of it can be discovered in the blood. As it exists in the animal body, it is nearly fluid, and is retained in minute cells: after death it is found solid, varying in solidity in different animals. To procure it free from the animal fluids and cellular fibre mixed with it, it is cut and washed in water, and is melted with a gentle heat, a little water being added, to prevent it from being scorched. Fat thus prepared, is named Axunge or Lard when soft; when of a firmer consistence it forms Tallow; and from some animals, as from the whale, and other marine animals, it is obtained fluid, forming Animal Oil.

Animal fat has properties nearly the same as those of vegetable expressed oil. It is insipid and inodorous, insoluble in water and in alkohol, is capable of combining with the alkalis, and forming soap; it is inflammable, and cannot be volatilized unchanged.

Fat, exposed to a warm atmosphere, is liable to become rancid. This rancidity appears to be owing to the absorption of oxygen, and consequent formation of an acid, either from the oxygenation of the fat itself, or of the gelatinous matter mixed with it. This acid may be abstracted by washing with water or alkohol, when the sweetness of the fat is in some measure restored, while the water acquires the power of reddening the vegetable colours.

Fat melts from a very moderate heat. By continuing the heat, or raising it above the melting point, it suffers decomposition, at a temperature of about 600°; pungent vapours arise from it; and when cold, it is found acrid and of a yellow colour. A similar decomposition is effected, by distilling it in close vessels: an acid liquor passes over, with an empyreumatic oil, partly liquid and partly concrete; carburetted hydrogen and carbonic acid gases are disengaged, and the residuum is mixed with charcoal: by repeating the distillation of the oily matter, a new formation of these products takes place, until the whole is decomposed. From the products of this decomposition, fat, like expressed oil, appears to be a compound of carbon, hydrogen, and oxygen. Ammonia is usually mingled with the products in small quantity; but if the fat has been well washed, it does not appear.

Fat is highly inflammable, and in burning gives much light; hence its use for this purpose; it is probable, that by the high temperature in the wick in the common method of burning it, it is decomposed and converted principally into a gas of the nature of olefiant gas, from the combustion of which the light originates. The products of this combustion, are water and carbonic acid.

Fat is acted on by the acids, the result being different according to the acid employed, and the manner in which it is applied. If nitric acid be added in small quantity, it is decomposed, its oxygen is abstracted by the fat, and what has been named by the French chemists Oxygenated Fat, is formed. The process has been received into the Pharmacopœia; it is to add to melted lard one-sixteenth of nitric acid, stirring them thoroughly, and keeping the mixture fluid for some time: nitric oxide and nitrogen gases are evolved, and the lard becomes granular and of a firmer consistence. If washed with water, any remaining nitric acid is removed: and a product is obtained of a waxy nature. By distilling nitric acid repeatedly from fat, Gren obtained acetic and oxalic acids. Vogel obtained what he considered as saccho-lactic acid: others have considered it as analogous to the sebacic acid formed from fat by heat. Sulphuric acid, even in small quantity, chars fat, rendering it brown or black, and producing a kind of decomposition, whence an oily product and a substance approaching in its properties to what is named Adipocire, are formed. Muriatic acid exerts little action upon fat.

Fat combines with the alkalis, forming saponaceous compounds.

Fat, like the expressed oils, is capable of combining with sulphur and with phosphorus, when their mutual action is aided by a moderate heat. It unites with a number of the metallic oxides, and forms with them compounds more firm than the fat itself. From its facility of oxidation, it can even be made to act on the metals. Thus, if copper be covered with grease, and left exposed to the air, its surface soon becomes green; and quicksilver triturated with lard, forms an ointment of a blue colour, which becomes deeper on keeping, and from which at length, according to the experiments of some chemists, scarcely any metallic quicksilver can be obtained; while, according to Vogel, it still exists in it with very little oxide *.

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* Nicholson's Journal, vol. xviii. p. 110.

A peculiar view of the nature of fat in its several varieties, has lately been brought forward by the French chemists, Chevreul and Braconnot. It is considered not as a homogeneous substance, but as composed of different principles, capable of being obtained apart. A short statement of this has been given under the history of the vegetable expressed oils, to which it also applies, (page 156-7), but it is to be stated more fully, as being more strictly connected with animal fat.

Chevreul had found, that in the process of saponification, the oil or fat, whether vegetable or animal, undergoes changes of composition by the action of the alkalis, in consequence of which new products are formed. And in prosecuting the investigation of these changes, he was led to the conclusion, that fats and oils are composed of two principles, one of a firm consistence, which is analogous to suet or tallow, the other more soft or liquid, analogous to vegetable oils. To the former of these he has since given the name of STEARIN, to the other that of ELAIN. He obtained them separate by submitting lard or fat to the action of boiling alkohol, employing alkohol of a specific gravity from 0.791 to 0.798, as exerting a more powerful solvent effect, than alkohol less highly rectified. On allowing the liquor to cool, the portion of fat dissolved is resolved into two combinations; one with an excess of stearin is deposited, the other with an excess of elain remains dissolved. The first is separated by filtration, and is again submitted to the action of boiling alkohol, until a solid matter is obtained fusible at 110°.

STEARIN thus procured, was from all the varieties of fat of a very fine white colour, inodorous or nearly so, insipid, and producing no effect on the colour of litmus: on cooling after fusion, it crystallized in fine needles; it varies in its fusibility, and likewise in its solubility in alkohol: it forms soap with the alkalis, but forms at the same time a portion of fluid, sweet, soluble in alkohol and water, and which appears to be what Scheele called the Sweet Principle of Oils.

Elain remains in the above process dissolved in the alkohol; the solution is submitted to cold, to precipitate as much as possible the stearin; it is then submitted to distillation, adding towards the end a little water; the elain remains. All the varieties of it obtained from the fat of different animals, are liquid at the temperature of 60, with a specific gravity of about 915; they are usually colourless and inodorous, but some of them have colour and smell from the adherence of foreign matter: they are all abundantly soluble in alkohol, dissolving in less than their own weight at a boiling temperature, and precipitating only partially on cooling: they combine with the alkalis, and form soaps, affording at the same time the sweet soluble matter like stearin, and nearly in the same proportion [*].

Braconnot obtained the same principles by a more simple process, in which there can be no supposition of any modification of composition by chemical action. It is founded on the physical property peculiar to oil, of being imbibed easily by soft paper: on pressing any oily or fatty substance rendered sufficiently solid by cold, between folds of bibulous paper, the fluid oil analogous to the elain of Chevreul is absorbed, while the concrete fat, or suet, as he names it, analogous to the stearin, remains untouched. To render the latter perfectly pure, it is melted with a little oil of turpentine, and when cold, is again pressed between soft paper; the last portions of oil are thus removed, and the pure suet remains. It varies somewhat in its physical properties and fusibility, as obtained from different fats: it is dry, and brittle, and is so far analogous in this respect to wax; after fusion, it breaks smooth and flaky, somewhat similar to spermaceti; it has a shining lustre, which it communicates to the fingers, or to paper; in some varieties it is semi-transparent or diaphanous; it melts at temperatures from 130 to 140 of Fahrenheit. It dissolves, though sparingly, with the assistance of heat, in alkohol, and more abundantly in ether. By the action both of acids and of alkalis, it suffers decomposition, being converted into a substance analogous to spermaceti, and into an oil, both soluble in alkohol. The fluid oil which exists along with the suet, and is absorbed by the paper in the above process, is obtained by placing the folds on warm water, on the surface of which it speedily collects. It is liquid, colourless, or with a yellow tinge similar to the vegetable expressed oils, but distinguished by not congealing readily: it combines with great facility with the alkalis. All fatty substances Braconnot supposes to be compounds of these in various proportions, and in no product is either of them pure. Butter consists of from 60 of oil and 40 of suet, to 35 of oil and 65 of suet, according to its quality; hog's lard of 62 of oil and 38 of suet; and marrow of 24 of oil and 76 of suet. Even the vegetable expressed oils have an intermixture of these principles, as has been stated under their history *.

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[*] Annales de Chimie, tom. xciv. xcv. Annales de Chimie et Physique, tom. ii.

In the process of saponification, by the action of the alkali, on the oils or fats, these principles suffer certain chemical changes; the alkali does not directly combine with them, but subverts their composition, forming two products somewhat analogous to acids, with which the alkali combines, and it is from this kind of resulting affinity that the change seems to arise. There is at the same time a formation of the substance denominated the Sweet Principle of Oils,—and these changes are effected not only by

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* Annales de Chimie, tom. xciii. Philosophical Magazine, vol. xlvi.

potash and soda, but likewise by the alkaline earths, and some of the metallic oxides, such as those of lead and zinc. Of these products, the one which Chevreul first obtained from soap, he named Margarine, from the form under which it appears of pearly scales, and considering it since as an acid, he has given it the name of Margaric Acid. The other he has named Oleic Acid. A view nearly similar of the changes which occur in saponification, has been given by Braconnot.

MARGARINE or MARGARIC ACID, the first of these products, was obtained by Chevreul, by submitting the soap formed by the action of potash on hog's lard, to the action of boiling water; the solution, on cooling, deposites a pearly matter, which is a super-margarate of potash, the liquor becoming at the same time alkaline, and retaining the oleic acid in combination with the alkali. The pearly matter being washed, is dissolved repeatedly in boiling water, to free it from any foreign matter; the liquor is filtered, and the precipitate it affords on cooling, is lastly washed with alkohol; it is then decomposed by muriatic acid, which combines with the potash, and the margaric acid being insoluble, is separated. This substance, obtained from different fats, is of a brilliant pearly whiteness, insipid, and nearly inodorous; it is lighter than water; melts at 135° of Fahrenheit into a colourless liquid, which crystallizes on cooling, in brilliant needles; by a higher heat it is volatilized and decomposed. It is insoluble in water; alkohol at a boiling heat, dissolves nearly twice its weight of it; the solution, in cooling, congeals in an entire mass; its several varieties differ merely in fusibility, melting at temperatures between 130° and 140°, and in the arrangement and size of the needles which are formed when cooled on the surface of water. The acidity of this substance is established by its reddening litmus, and combining with and neutralizing the alkalis. With potash it forms a soft and pearly-like matter, not sensibly alkaline, insoluble in water, and soluble in boiling alkohol; it also forms a compound with an excess of alkali, containing twice the quantity existing in the first. It combines also with the other bases. All these compounds are more analogous to soaps, than to salts *.

OLEIC ACID. In the preceding process for obtaining margaric acid, the oleic acid remains in solution with a portion of potash. To obtain it, the liquor was neutralized by tartaric acid; a portion of super-margarate of potash is deposited, and the alkali again becomes in excess; it is again neutralized by tartaric acid: these operations are repeated until no pearly like matter is precipitated; the oleate of potash is then decomposed by a farther addition of tartaric acid. The oleic acid is an oily-like fluid, lighter than water, which preserves its fluidity at temperatures near the freezing point of water; it congeals in crystalline needles; it is not easily obtained perfectly pure, and hence has frequently colour and odour; it is insoluble in water, soluble in alkohol; reddens litmus, and combines with the different salifiable bases, forming compounds somewhat analogous to soaps, the composition of which has been given by Chevreul †.

SEBACIC ACID, the acid formed from the decomposition of fat by heat, was observed by Bergman to resemble in its saline combinations the acetic; Gren considered it as the same with that acid; but as it presented some differences, it continued in general to be regarded as a peculiar acid. Various processes were given for preparing it,

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* Annales de Chimie, tom. lxxxviii. Philosophical Magazine, vol. xliv.

† Ibid. tom. xciii. xciv. Annales de Chimie et Physique, tom. v.

of which one proposed by Guyton has been usually followed. Fat is melted in an iron pot over a naked fire; quicklime in powder is added to it, stirring it continually, and increasing the heat. When the mixture has cooled, on boiling it in water, a brown acrid salt is obtained by evaporation of the solution, which was considered as the sebate of lime; by exposing it to heat in a crucible, any adhering oily matter is decomposed, and the salt is obtained pure and white, by solution and crystallization. If sulphuric acid be poured on it, the sebacic acid is disengaged, and being volatile, may be obtained by distillation. The acid is formed in this process, by the decomposition of the fat by the high temperature, and is prevented from being dissipated by its combination with the lime. As obtained by distillation, it is a liquid having an acrid suffocating odour, exhaling a white vapour when in a concentrated state, and having somewhat of an oily appearance. It reddens the vegetable colours, is volatile, and, when transmitted through an ignited tube, is resolved into water, carbonic acid, carburetted hydrogen, and charcoal. Its salts, which were named Sebates, are in general soluble and crystallizable.

Thenard, from a more recent examination of this acid, has revived the opinion, that it is merely acetic acid, the pungency of its odour being probably derived from a little sulphurous acid *. According to this chemist, there is, however, a real sebacic acid. It is obtained by distilling lard, and treating the product with hot water: acetate of lead is added to the liquor: a flaky precipitate is formed, which is dried, and heated in a retort with sulphuric acid. The liquid condensed had no acidity; but there floated on the matter in the retort a substance like fat, which was separated, washed, and boiled with water. The water dis-

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* Nicholson's Journal, 8vo, vol. i. p. 34.

solved it; and, by refrigeration, crystalline needles were deposited, acid, and possessed of peculiar properties. They were also procured, by treating distilled fat with water, filtrating and evaporating the liquor. This acid, which Thenard regards as the Sebacic, is without smell: its taste is slightly acid: it reddens tincture of turnsole, and is more soluble at a high than at a low temperature: boiling water saturated with it even becomes concrete by refrigeration: alkohol dissolves a large quantity of it: it crystallizes in small needles, or in large plates, of a brilliant appearance. It precipitates acetate and nitrate of mercury and of lead, and nitrate of silver: it neutralizes the alkalis, and forms with them soluble salts: that with potash does not attract moisture from the atmosphere; has little taste, and is decomposed by sulphuric, nitric, or muriatic acid. It does not render turbid solutions of lime, barytes, and strontites. With the production of this acid, there is also a formation of acetic acid, which may be obtained by saturating the product of the distilled fat with potash, and decomposing it by sulphuric acid. According to Berzelius, the sebacic acid of Thenard is impure benzoic acid.

Spermaceti differs in some of its qualities from fat. It is found in the head of a species of whale, the Physeter macrocephalus, in an unctuous mass, from which a quantity of oil is obtained by expression. There remains a flaky substance, which is purified by melting, washing with water and with a weak alkaline solution. This is Spermaceti. It also exists in the oils of other species of whale, and is often spontaneously deposited.

Spermaceti is in masses of a flaky crystalline texture, soft, but brittle, white, and brilliant. It is less fusible than fat; its melting point being 113°. By raising the heat, it may be volatilized, and passes over by distillation with little alteration; but by subjecting it to this repeatedly, it is decomposed, a quantity of acid is evolved, and a liquid oil is formed. The products of its decomposition are similar to those of wax, and its composition appears, from their comparative analyses by Gay Lussac and Thenard, to be nearly the same.

Spermaceti is inflammable, and burns with a clear flame, and has nearly the same superiority as wax for artificial illumination.

A property in which it differs from fat and expressed oil, is its solubility in alkohol and ether. In alkohol it is dissolved very sparingly. According to Dr Bostock's experiments, 100 grains of alkohol dissolve only .52 grains, half of which precipitates on cooling. Warm ether dissolves it rapidly; and by cooling it is precipitated so abundantly, as in appearance to convert the whole into a solid crystallized mass *. It is dissolved with facility by oil of turpentine gently heated, and is deposited as it cools.

The alkalis act on spermaceti, and form soaps, less perfect, and less soluble in water, than the soap from fat. A solution of pure potash dissolves it, and the compound is soluble in warm water. Ammonia does not act on it when cold, but when boiling unites with it, and forms an emulsion, not decomposed by cooling or by the addition of water, but only by an acid †.

The acids have little effect on it; concentrated sulphuric acid dissolves it, and changes its colour; and water precipitates it from this solution.

In its properties this substance bears a resemblance to the matter which principally composes biliary calculi, and to that which is formed by the slow decomposition of muscular fibre,—a matter which Fourcroy distinguished by the name of Adipocire, as being intermediate between

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* Nicholson's Journal, vol. iv. p. 134.

† Bostock, Nicholson's Journal, vol. iv. p. 134.

fat and wax. The last substance, Chevreul remarks, is not homogeneous, but is rather a species of soap containing margaric acid, in combination with oil. Spermaceti and the matter of biliary calculi are homogeneous; but although they have a general resemblance, they differ remarkably in the circumstance, that the latter cannot be converted into soap by the alkalis. Spermaceti suffers this change; and in conformity to his general theory of saponification, Chevreul considers this as consisting in the production of acid, with which the alkali combines. He has accordingly described the properties of an acid procured from this combination, by the soap of spermaceti being decomposed by an acid. It is concrete, white, easily fusible, but when cooled does not assume the plated structure of spermaceti: it is insipid and inodorous; insoluble in water, but abundantly soluble in boiling alkohol, from which it consolidates on cooling; it reddens faintly the colour of litmus, and combines with alkaline bases. Chevreul has given it the name of CETIC ACID, from CETINE, a term which he has applied to spermaceti *.

SECT. XVII.—OF THE CEREBRAL PULP.

THE soft matter which constitutes the brain and nerves, is different, in its physical qualities, from any other animal substance. It was examined by Fourcroy, with the view of determining its chemical characters †, and more lately by Vauquelin and John.

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* Annales de Chimie, tom. xciv. Annales de Chimie et Physique, tom. ii.

† Annales de Chimie, tom. xvi.

In its consistence it is soft and pulpy: it soons suffers spontaneous decomposition when exposed to the air, but, when immersed under water, remains long without much change. Dried by the heat of a water-bath, it coagulates, and a little water separates from it. When urged with a strong fire, it exhales ammonia, swells, becomes black, melts, and diffuses acrid fumes: it inflames if the air is admitted, and sulphurous acid is formed from its combustion. When decomposed in close vessels, the products are oil, carbonate of ammonia, carburetted and sulphuretted hydrogen, and carbonic acid gases, with traces of phosphates of lime and soda in the residual charcoal.

When the cerebral pulp is diluted with water, it is coagulated by heat; the liquor separated from the flocculi gives a precipitate with lime-water, and affords phosphate of soda by crystallization. Alkohol produces coagulation; as do the acids; indicating, therefore, a principle analogous to albumen. Sulphuric acid, in coagulating it, reacts upon it, an oily matter being evolved. Nitric acid diluted disengages nitrogen gas; and phosphate and oxalate of lime, and oxalate of soda, are found in the residual liquor. Muriatic acid produces coagulation; and the ley affords salts, the bases of which are soda and lime, neutralized partly by muriatic, partly by phosphoric acid.

The alkalis dissolve this matter. Potash acts upon it in the cold, causing an evolution of ammonia: when heat is applied, the compound is saponaceous.

By the action of alkohol, not only is the matter analogous to albumen separated, but another substance is obtained, similar to some of the varieties of adipocire. The alkohol being repeatedly applied hot to the cerebral pulp previously dried, was found by Fourcroy to deposite each time on cooling brilliant laminæ of a yellowish white colour. This substance was of an unctuous appearance, softened at the heat of boiling water, but did not melt.

At a higher temperature it acquired a darker colour, and exhaled, during its fusion, an empyreumatic ammoniacal odour.

Vauquelin submitted the substance of the brain to the same mode of analysis by alkohol, aided by a boiling heat. The liquor deposited on cooling first a portion of a fatty matter in plates, white, of a silky lustre, staining paper like oil, fusible, and thus becoming solid, with some tenacity, and of a brown colour. By evaporation of the alkohol to one eighth part, another oily matter separated, fluid and of a yellow colour; on drying it by exposure to the air, it becomes red, has an odour similar to that of the brain, and a taste like rancid fat; it forms an emulsion with hot water, and dissolves in hot alkohol, the greater part of it separating on cooling; it blackens when heated, and melts; it appears to be the same as the preceding fat, with an intermixture of the next substance to be described. This remains after the separation of the two oily substances from the alkoholic solution, forming a liquor of a brownish yellow colour, which has the taste and smell of the juice of meat, and which by evaporation affords a solid matter, brown and deliquescent, soluble in alkohol, and forming with tannin an insoluble combination. It is the same substance as that to which Rouelle had given the name of Saponaceous Extract, and Thenard that of Osmazome. There remains a large portion of matter insoluble in alkohol, in the form of greyish white flocculi, and which Vauquelin regards with Fourcroy as albumen. Lastly, there are detected in the analysis small portions of phosphates of potash, lime, and magnesia, and muriate of soda. Vauquelin also inferred the presence of phosphorus in its entire state, combined with the fatty matter of the brain, from finding, that when this matter had been extracted by alkohol, the residue obtained on evaporation afforded phosphates by its combustion, though no phosphoric acid was to be discovered in the solution itself. He also found traces of sulphur. He gives the following as the whole composition: water 80, white fatty matter 4.53, red fatty matter 0.7, albumen 7, osmazome 1.12, phosphorus 1.50, acids, salts, and sulphur 5.15 *.

Dr John, prosecuting Vauquelin's investigation, was led to conclude, that phosphorus is not a constituent of the brain, but only phosphate of ammonia. The other results he finds similar to those given by Vauquelin, with the addition of a trace of sulphate of potash, and phosphate of iron †.

Fourcroy had found the matter of the nerves to be the same as that of the brain. According to Vauquelin, it contains less fatty matter and more albumen. The medulla elongata and spinal marrow, on the contrary, contain more fatty matter, and less albumen, osmazome, and water. The substance of the nerve yields a small portion of matter to the successive action of alkohol and water, and the remainder dissolves almost completely in caustic potash.

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* Annals of Philosophy, vol. i. p. 532.

† Ibid. vol. vii. p. 55.

CHAP. III.

OF THE SPONTANEOUS CHEMICAL CHANGES, AND THE DECOMPOSITION OF ANIMAL SUBSTANCES.

THE elements of which the animal products are formed, having energetic affinities, the operation of which is farther favoured by the state of condensation in which they exist, they are extremely liable to re-act on each other, and to enter into new combinations, whence the existing composition is destroyed. This may take place either at natural temperatures, or at temperatures more elevated; and according to either of these circumstances, the kind of decomposition, and the new combinations that are established, are different. In concluding the history of animal substances, both species of spontaneous decomposition are to be considered.

SECT. I.—OF THE DECOMPOSITION OF ANIMAL SUBSTANCES AT A HIGH TEMPERATURE.

WHEN the composition of any animal substance is subverted by heat, its elements enter into binary or ternary combination. Nitrogen and hydrogen being usually present in largest proportion, portions of them combine, and form ammonia. Another portion of the hydrogen enters into combination with carbon and oxygen, forming empyreumatic oil, acid, and oxycarburetted hydrogen gas. Oxygen and carbon unite and form carbonic acid, with which the ammonia combines; and sulphur and phosphorus, which are generally in greater or less quantity constituents of animal matter, uniting with hydrogen, and probably also with certain proportions of nitrogen and oxygen, form those gases, having a fœtid odour, the evolution of which peculiarly marks the decomposition of animal matter. The residual charcoal contains salts, having lime, magnesia, and soda for their bases, combined with phosphoric, sulphuric, muriatic, and carbonic acids, and also oxide of iron.

But besides these, which require no farther observations, a product is formed from the decomposition of many animal substances by heat, the Prussic Acid, the chemical history of which remains to be given. It exists, as has already been stated, (page 302.), in the vegetable kingdom, but, as obtained from animal substances, it is the product of their decomposition by heat, and it is from this source that it is always procured for chemical purposes.

A rich pigment has been long known under the name of Prussian Blue. It is prepared by drying blood, mixing three parts of the dried residuum with two parts of the potash of commerce, and calcining the mixture in a crucible by a red heat, as long as any vapours exhale; it is then boiled in successive portions of water, which are afterwards mixed together, and concentrated by evaporation. A solution is prepared of one part of sulphate of iron, and two parts of alum; and to this the liquor obtained from the calcined blood and alkali is added, as long as any precipitate is formed. This precipitate is of a green colour, but by washing it with a little dilute muriatic acid, it becomes of a dark rich blue colour. This forms the prussian blue of commerce.

Much attention has been bestowed on the investigation of the nature of this substance. At an early period, after

Woodward, in 1724, had made public the process, Brown and Geoffroy shewed, that other animal substances besides blood, as flesh, wool, &c. calcined with potash, furnished a ley capable of forming prussian blue. Macquer made the important discovery, that the property of forming the colour depends on a principle combined with the alkali; that in the formation of the prussian blue, this combines with the iron, and that it may be again abstracted from it by boiling in an alkaline solution; it is thus transferred to the alkali, which hence acquires the power of again forming the precipitate of prussian blue, from a solution of sulphate of iron. He shewed likewise, that the reason the precipitate is green, is, that the liquor containing an excess of alkali throws down a portion of yellow oxide of iron, which mingles with the blue precipitate, and muriatic acid gives the deep blue colour, by dissolving, and thus removing this oxide. Scheele completed the investigation, and obtained the colouring principle in a separate state. He had found, that when the liquor prepared from calcined blood and potash is exposed to the air, it soon loses its power of precipitating iron blue; and that, when a quantity of this liquor is put into a vessel filled with carbonic acid gas, paper dipt in a solution of sulphate of iron attached to the cork, is soon covered with precipitated oxide of iron, and when wetted with muriatic acid, assumes a blue colour. These facts appeared to prove, that acids attract the alkali more strongly than the colouring matter does, and that this matter is volatile; and hence he inferred, that it might be obtained by distillation. He therefore put a quantity of the alkaline liquor impregnated with it, into a retort, with an excess of sulphuric acid, and distilled with a gentle heat. The water which came over had a peculiar smell and taste, and produced with oxide of iron prussian blue. Exposed to the air for some hours, it lost this property, the colouring principle being dissipated.

Scheele found it difficult to transfer, by single affinity, the colouring matter from prussian blue; for although the alkalis attract it, a portion of oxide of iron accompanies it; and hence these compounds, as he remarks, are triple compounds, consisting of alkali, a little iron, and the colouring matter. With that skill, however, which eminently marked all his investigations, he discovered a process by which the transfer might be effected. Two ounces of prussian blue, and one ounce of red oxide of quicksilver prepared by nitric acid, are put into a flask, with six ounces of water, and boiled for some minutes, with constant agitation. It is then poured on a filtre, and the matter which remains on the paper is lixiviated with two ounces of hot water. The liquid which has passed through, is a combination of the colouring matter with oxide of quicksilver, without any oxide of iron. This he found could not be decomposed by acids, alkalis, or lime; and the colouring matter could be separated only by reducing the mercurial oxide to the metallic state. To effect this, the filtered solution, from the above quantities of materials, is poured on an ounce and a half of iron-filings, free from rust, to which are added three drachms of sulphuric acid. Hydrogen gas is thus disengaged, and acting in its nascent state abstracts the oxygen of the oxide of quicksilver. The clear liquor, after the action has ceased, is poured off and distilled. When the fourth part has come over, the whole of the colouring matter is obtained, as it is more volatile than water, and rises first. There is a slight contamination of sulphuric acid, which may be removed by distilling from a little chalk *. This principle he regarded as an acid, and named Acid of Prussian Blue, a name changed by Guyton to that of Prussic Acid.

Proust found, that the prussiate of mercury formed in the preceding process, though not decomposed by the other acids, suffers decomposition from the muriatic, and

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* Scheele's Chemical Essays, p. 519.

the prussic acid is expelled. He also found, that it may be disengaged from prussian blue by diluted sulphuric acid, and by the application of heat is discharged in the gaseous form. By connecting the retort in which this process was performed, with a bell jar containing alkohol, over quicksilver, he received the gas over the alkohol, which absorbed it rapidly. Water placed in an intermediate receiver, was also surcharged with it, and solutions were procured, having the odour of the prussic acid extremely strong, and from which the gas constantly tended to escape *.

Gay Lussac, employing the process of decomposing prussiate of mercury by muriatic acid, with some additional precautions, has been enabled to procure prussic acid in a purer form, and has thus been enabled better to determine its properties. The prussiate is put into a retort, to the neck of which a curved tube is adapted, the other end of which terminates in a two-necked bottle, containing a little chalk and muriate of lime, the chalk being intended to attract any muriatic acid that might pass over, and the muriate of lime to absorb water. This is connected with a second similar bottle, containing also muriate of lime; and from this a bent tube issues which is inserted in a phial designed to receive the prussic acid; and the whole are kept cool by being surrounded with ice and salt: or by a simplification of the apparatus, introduced by Gay Lussac in his subsequent researches, the chalk and the muriate of lime may be disposed in successive portions of a long horizontal tube, terminating in a small receiver kept cool. Fuming muriatic acid is poured on the prussiate in the retort, and a gentle heat is applied; the prussiate dissolves, and the liquid soon appears to boil. Vapours pass over, which partly condense in the neck of the retort in streaks like alkohol; and the process is stopt as soon as water is ob-

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* Annales de Chimie, tom. lx. Philosophical Magazine, vol. xxxiii. p. 46.

served to rise. The prussic acid condenses almost entirely in the first bottle; or in the first part of the tube, when a tube is employed, from which, by a slight heat, it may be volatilized into the receiver; it is a little coloured; but it is freed from this by a second distillation; and it is so volatile that this may be done by a heat, not exceeding 95°, being applied around the bottle in which it is condensed; it rises in vapour from the muriate of lime, and is condensed in the second; and by removing the communication between these, and applying again a gentle heat, it may be volatilized and condensed perfectly pure in the phial designed to collect it *.

It had been observed, as already stated, that this acid exists in the gaseous state. Gay Lussac, in employing the preceding process, having connected the retort with an inverted jar filled with quicksilver, according to the experiment originally made by Proust, obtained a large quantity of elastic fluid, having the strong smell of prussic acid. The temperature of the room was 68°; but afterwards at a temperature of 53°, it was observed that the volume of the gas had diminished greatly, and that a liquid condensed in the jar. This shewed the volatility of the prussic acid, and at the same time that it can be condensed in the liquid form. Gay Lussac accordingly found, that it is a liquid more volatile than ether. It boils at 80° of Fahrenheit, and evaporates rapidly at a lower temperature, so that it cannot be poured from one vessel to another without loss: it hence also enlarges greatly the volume of atmospheric air, or of any other elastic fluid. The specific gravity of its vapour is 0.9476, air being 1.

In its liquid state it is transparent and colourless as water; its specific gravity at 45° of Fahrenheit, is 0.705; its taste is at first cool, but soon becomes acrid and irritating,

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* Annales de Chimie, tom. lxxvii. Nicholson's Journal, vol. xxxi.

Its odour is strong, resembling that of the peach blossom or bitter almond, which appear indeed to derive their odour from it, as well as their narcotic property, as has been already stated in enumerating it as a product of the vegetable system. The narcotic power of the acid is extremely strong; a few drops of it, in its concentrated state, given to small animals, causes instant death; a single drop even applied to the tongue is sufficient; the same effect is produced by exposing them to its vapour, and this even without immersion in it, but merely applying the nostrils to a vessel containing it; and a German chemist is said to have lost his life from a quantity of it having been dropt on the naked arm *.

It is singular that this liquid acid, though so volatile, can be congealed by a cold which is not very intense. Gay Lussac found that its congelation takes place when it is exposed to a freezing mixture of two parts of ice, and one of sea-salt, and it often forms regular prismatic crystals. It remains solid at —5°, but above this it liquefies. From this susceptibility of congelation, combined with its great volatility, arises a singular phenomenon. If a drop of it be exposed to the air at the extremity of a glass rod, or on a bit of paper, it instantly freezes. This is the only example of the congelation of a liquid by the degree of cold produced by its own evaporation under exposure to the atmosphere; as among all the volatile liquids there is none that freezes at a temperature so little remote from that of its vaporific point.

It has been considered as doubtful whether this substance can be regarded as an acid. Its taste, Scheele remarked, is not sour, but approaches to sweet; it has been generally believed not to redden paper tinged with litmus; and it has scarcely the most important acid character, the power

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* Annales de Chimie, tom. xcii. p. 52. Philosophical Magazine, vol. xlv. p. 76.

of neutralizing the alkalis and earths, and of forming with them crystallizable salts; at least it distinctly acquires this power, as Berthollet remarks, only when a metallic oxide enters also into the combination. It has only the remaining acid characters, of being soluble in water, decomposing soap, and precipitating alkaline hydro-sulphurets; and hence, as the same chemist has observed, the name of acid can be given to it, rather from the properties it displays in its ternary combinations, than from those it has in its insulated state. The observation, however, of its not reddening litmus paper, appears to have arisen from its not having been obtained in a pure form, and from its volatility. Gay Lussac has stated, that even when it has been rectified by repeated distillation from chalk, it faintly reddens litmus paper; but this is evanescent, from the speedy escape of the acid.

This acid in the gaseous state is inflammable. Like other substances of animal origin, it is decomposed at a high temperature; though less readily, as is evident from the fact, that it is formed only at the temperature of ignition. According to Bucholz and Proust, it suffers spontaneous decomposition in its watery solution. This decomposition Gay Lussac has found to take place rapidly even in well-closed vessels, where no air is present; it assumes a brown colour, which gradually deepens, and at length deposites a considerable carbonaceous residue, which gives a deep colour both to water and acids, and gives out a strong smell of ammonia. This ammonia has been formed in the decomposition, and is combined with a portion of the acid.

Prussic acid combines with the alkalis and earths; but its affinity to them is inconsiderable, and the acid is so liable to decomposition, that the constitution of these compounds is easily subverted, water even producing their decomposition. They are denominated Prussiates, and are obtained by combining the acid obtained by the process of Scheele with the different bases. They have been little examined;

a few observations only having been made with regard to them by this chemist *. With the fixed alkalis, he remarks, prussic acid forms compounds in which the alkaline properties are scarcely neutralized; for although the compound contains an excess of the colouring matter, it still restores the blue colour of paper reddened by an acid. By distillation, the prussic acid is partly separated from it, and partly decomposed; and it is decomposed by all the acids, even by the carbonic. With ammonia a salt is formed, which has still the ammoniacal odour, even when the colouring principle is in excess; it crystallizes in small prisms; this salt rises by distillation, nothing but pure water remaining in the retort. The aqueous prussic acid dissolves but a small quantity of barytes; with lime it presents nearly the same results as with the alkalis, combining with it, and the compound being decomposed by heat, as well as by carbonic acid, on exposure to the air. Magnesia is dissolved by it in small quantity, but by exposure to the atmosphere is again precipitated. Alumina is not dissolved in any sensible quantity.

Prussic acid has no sensible action on metals; but it acts on the oxides of many of them: and it is a singular fact, that its affinities are more powerful in these combinations, and hence the constitution of the acid is better preserved, than in its combinations with the alkalis and earths. With oxide of gold it forms a white compound; oxide of silver, precipitated by an alkaline carbonate from its nitrous solution, yields its carbonic acid with slight effervescence from its action; oxide of quicksilver is dissolved, and the solution crystallizes in four-sided prisms; oxide of copper assumes a citron colour, and oxide of cobalt a yellowish brown. The oxides of iron, tin, lead, and indeed the greater number of the other metals, are not directly affected by it. It decomposes, however, some of the metallic

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* Chemical Essays, 2d Dissertation on Prussian Blue.

salts: from a solution of nitrate of silver, a white powder is thrown down; from carbonate of iron, a precipitate at first of a sea-green colour, which changes to a blue; and from nitrate of mercury, a black powder. By boiling red oxide of mercury, either with prussiate of potash, or with prussian blue, the prussic acid combines with the oxide of mercury; and if the boiling be repeated several times with the mercurial oxide, the whole, or nearly the whole of the oxide of iron is separated; and a prussiate of mercury is obtained, which crystallizes, and which is not decomposed by the alkalis, or by sulphuric or nitric, but only by muriatic acid. This is, of any of the combinations of prussic acid, therefore, the one which best displays its acid powers. It consists, according to Mr Porret, of 13.8 prussic acid, and 86.2 red oxide of mercury. Gay Lussac, however, considers it under a very different point of view. He finds, that when prussic acid vapour is passed over the red oxide of mercury, water is formed; the acid must therefore be decomposed, its hydrogen combining with the oxygen of the oxide, and the solid product, the Prussiate of Mercury as it was named, consists of the compound radical of prussic acid, the cyanogen of Gay Lussac, with metallic quicksilver, or, in his nomenclature, is a cyanuret of mercury. Correcting Mr Porret's analysis by this view, it consists, he infers, of 79.91 of mercury, and 20.1 of cyanogen: but this correction is doubtful. It yields a portion of cyanogen by heat, and then becomes a sub-cyanuret.

By complex affinity, more striking effects are produced on the metallic salts. In examining these, Scheele employed prussiate of lime; and he gives the following enumeration of the changes it occasions. A solution of it being poured into a solution of gold, a precipitate is thrown down in a white powder, which is re-dissolved when the prussiate is added in excess, forming a colourless solution. The solution of platina is not changed; that of silver is precipitated of a white colour, and of a consistence like that of cheese; the precipitate being re-dissolved by an excess of the prussiate, and the combination in this case being so intimate, that it is not decomposed by muriatic acid. Mercury is precipitated from its nitrous solution in the form of a black powder. Sulphate of copper is precipitated of a citron colour; the precipitate being re-dissolved by an excess of the prussiate, and forming a colourless liquor, as it does also when submitted to the action of liquid ammonia. Sulphate of zinc gives a precipitate of a white colour; and this, unlike the greater number of these precipitates, is soluble in acids. Sulphate of iron is precipitated first of a yellowish brown colour, which soon changes to green, and then becomes blue on the surface, as it does also immediately on adding an acid. From acetate of lead, a white powder is precipitated: from the solution of cobalt, a powder of a brownish yellow colour; neither of these being re-dissolved by an excess of acid. Similar compounds are established by prussiate of potash added to the metallic solutions, of which Proust has given an account. The greater number of them are triple combinations; the prussic acid, with part of the salifiable base, entering into combination with the metallic oxide, the prussic acid having a tendency to form such ternary combinations: hence, as Berthollet has remarked, the supernatant liquid retains an excess of acid, though the prussiate by which the metallic salt is decomposed contains more alkali than is requisite to its saturation, and the precipitate weighs more than it would do if the oxide alone were combined with the prussic acid. And when the prussiate of potash and iron is used, it appears, from Proust's elaborate examination of the prussiates *, that a portion of iron also enters with the other metallic oxide into the combination. These triple combinations of prussic acid with an alkaline base and metallic oxide, are more permanent than the pure

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* Philosophical Magazine, vol. xxxiii. p. 42.

prussiates, the metallic oxide exerting such an affinity to the prussic acid as to preserve it from decomposition; and the alkaline properties are completely neutralized: many of them also can be crystallized.

Of these combinations, those with oxide of iron are of importance, from their use as chemical tests, and as forming prussian blue. Prussian Blue, it has been already stated, is prepared by adding the ley obtained from calcined blood and potashes, to a solution of sulphate of iron. The ley contains the prussic acid combined with the potash, the acid unites with the oxide of iron of the sulphate, and forms the blue precipitate, a little muriatic acid being employed to remove a green tint from the presence of a portion of oxide of iron, thrown down by an excess of alkali in the ley. The prussian blue of commerce also contains a portion of argillaceous earth, derived from a quantity of alum, dissolved along with the sulphate of iron, previous to the precipitation of this by the addition of the ley from calcined blood and potash; it serves the purpose merely of diluting the deep colour, and giving more consistence to the pigment. Some chemists have supposed, that a portion of the potash of the prussian ley enters with the prussic acid into combination with the oxide of iron. But, according to Proust, this is not the case, pure prussian blue leaving no saline matter by decomposition *.

The state of combination of the prussic acid with oxide of iron, is considerably influenced by the state of the metal with regard to oxidation, as Proust more particularly

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* The manufacture of prussian blue is attended with a very fœtid odour, from the drying and calcining the blood, which spreads to a considerable distance. It may be obviated by conducting the vapour through a tube issuing from a dome placed over the calcining vessel, and causing it to burn. Another apparatus has been invented by D'Arcet, described in Nicholson's Journal, vol. xxxiii. p. 268.

pointed out *. If the iron is in combination with an acid at the minimum of oxidation, the precipitate formed, by adding the common prussiate of potash and iron, is of a white colour, but from exposure to the air, it rapidly acquires a blue shade; or, if the metal be at a higher state of oxidation, the precipitate is at the first blue. These compounds seem to be of uniform composition, though often modified in their production by intermixture, or by an excess of oxide of iron. The white precipitate seems to consist entirely of prussic acid and black oxide of iron. The blue precipitate requires for its production, as Proust shewed, the iron in the state both of the black and the red oxide. In the prussian ley, or prussiate of potash and iron, by the action of which, on a salt of iron at the maximum of oxidation, the blue precipitate is formed, there exists a portion of black oxide of iron as an essential constituent; and in the formation of that precipitate, this black oxide enters with the prussic acid into combination with the red oxide of the salt. Hence it cannot be formed by the combination of prussic acid with the red oxide alone. Proust found, that 100 of the blue precipitate yield by incineration 55 of red oxide of iron; but of this only 35 preexisted in it, the remainder being in the state of black oxide,—100 parts, according to Mr Porret's analysis, consist of 34.05 prussic acid, 19.33 black oxide of iron, 35 red oxide, and 11.62 of water. Gay Lussac considers it as doubtful, whether it is a compound of prussic acid with oxide of iron and water, or consists of the compound radical of prussic acid, cyanogen, with metallic iron,—that is, in his nomenclature, a cyanuret of iron. The white precipitate in this case would be a sub-cyanuret of iron in combination with hydro-cyanic or prussic acid.

When an alkaline solution, as of potash, is boiled on prussian blue, it abstracts the greater part of the prussic

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* Nicholson's Journal, 4to, vol. i. p. 454; 8vo, vol. xvii.

acid, with a portion of oxide of iron, and forms a soluble compound, a prussiate of potash and iron. This salt may be obtained by evaporation in octahedral crystals of a yellowish colour. It is abundantly soluble in water. The iron exists in it altogether in the state of the black oxide, and is retained by so powerful an attraction, when not in excess, that it is not abstracted by the succinates, the hydro-sulphurets, or other re-agents, by which it is usually discovered. The composition of the salt had been imperfectly determined. Proust found, that in 100 parts there exist 17 of black oxide of iron, with 10 of water. Mr Porret, by a more complete analysis, has given as its composition in its crystallized state, black oxide of iron 17.26, potash 39.34, prussic acid 30.40, water 13.

This salt, under different forms, has been much used by chemists as a test to discover the presence of iron. It is of great delicacy, from the deep colour which it strikes with the iron at the maximum of oxidation; but from the iron it contains, it is liable to fallacy; for if any free acid be present, or be evolved in the application of the test, this re-acts upon it, and gives rise to a precipitate of prussian blue, indicating, of course, iron to be present when it is not; and increasing the quantity of it when it is. It has been endeavoured to remove this source of fallacy, by freeing it from this portion of iron; but this is impracticable. Richter and Bucholz clearly shewed, that the presence of the oxide of iron is essential to preserve the constitution of the prussic acid; that the compound of this acid and the alkali alone, can be formed only in the dry way, and at the temperature of ignition: when it is dissolved in water, it is immediately decomposed; part of the prussic acid escapes, and, from the smell of ammonia produced, part appears to be decomposed: and it is only from the presence of oxide of iron that the permanent combination is established. All the precipitates produced by means of the test prepared in the usual method, they conclude, contain iron, and are different in their colour from those where the iron is not present *.

When the compound contains, however, only a certain quantity of the oxide of iron,—that essential to its constitution, this exists in the combination with such force of attraction, that even a free acid does not subvert it; and therefore, a triple prussiate of this nature may be formed, which may be employed with more accuracy as a test of iron. The liquor which is prepared from the mixture of blood and pearl-ash calcined, is, under this point of view, preferable to that prepared from the action of an alkaline ley on prussian blue; for although the former contains a portion of oxide of iron derived from the blood, it is much less considerable than that which the latter contains. The proportions, according to Bucholz, which answer best in preparing the triple prussiate with this view, are two parts of dried blood with one of carbonate of potash; this mixture being heated to redness in a crucible, and being kept in a state of ignition for three quarters of an hour after the flame that appears at the surface has ceased. This, dissolved in water, affords a liquor which contains only a small quantity of iron, and which, dropt into muriatic acid, affords no blue, but only a white precipitate †. Richter has given a similar process, the ley from the calcined blood, and alkali, being purified by adding acetate of potash as long as any precipitate is thrown down, and the prussiate being obtained by crystallization ‡.

Even the common solution of triple prussiate of potash, and iron prepared by digesting an alkaline solution with prussiate of iron, may be so far freed from the metal as to be used as a test. According to Berthollet, the abstraction of the excess of oxide of iron may be effected by cal-

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* Nicholson's Journal, vol. ix. p. 278. Ann. de Chim. li. p. 180

† Nicholson's Journal, vol. ix. p. 280.

‡ Annales de Chimie, tom. li. p. 183.

cining slightly the crystallized prussiate, and again crystallizing it. Another process employed by Klaproth has been described by Kirwan *. The liquor is filtered, and any excess of alkali is saturated by the addition of sulphuric acid; (or, as Richter proposed, by acetate of lime:) it is poured off clear from a precipitate which is thrown down, and is evaporated, so that, when set aside, it shall crystallize: crystals of a cubic form and of a yellowish colour are found mingled with crystals of sulphate of potash, and with oxide of iron. The former are picked out, and re-dissolved in water: any sulphuric acid that may be present is removed by the addition of barytic water, and it is again made to crystallize. These crystals are dried and kept for use: if they receive no bluish tinge when wetted with muriatic acid, they may be considered as sufficiently pure to be employed as a test.

Dr Henry has given another process †. To a solution of potash heated nearly to boiling, prussian blue is added until its colour cease to be destroyed. The liquor is filtered, and there is added to it, while warm, a little dilute sulphuric acid, continuing the addition by successive portions, until no blue precipitate is thrown down. A solution of sulphate of copper, in 6 parts of water, is poured warm into the clear liquor poured off from the blue precipitate, as long as a reddish brown sediment appears. This is prussiate of copper; it is to be washed with warm water until the water come off colourless. This precipitate, when dry, is to be added to a solution of pure potash; the prussic acid leaves the oxide of copper, and combines with the alkali, forming a prussiate as free from iron as can be prepared.

The test, as prepared by any of these processes, always contains a quantity of oxide of iron; and although, from

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* Elements of Mineralogy, vol. i. 494.

† Epitome of Chemistry, p. 250.

the strong attraction with which this is retained, it may be used without much fallacy to discover the presence of iron, it cannot be employed to determine its quantity, from the precipitate which it throws down from any liquor containing this metal; at least without allowance being made for the quantity the test does contain. This is done by decomposing 100 grains of the crystallized prussiate, by exposure to a strong red heat, discovering what quantity of oxide of iron remains, and from this, by knowing what quantity of the salt has been employed in the precipitate, determining what quantity of the iron which it indicates has been derived from this source. In general, the crystallized salt, as prepared by these methods, contains from 22 to 30 in 100 parts of oxide of iron. According to Mr Porret, 100 parts of the blue precipitate, washed and dried, may be considered as equivalent to 34.24 of red oxide of iron in the solution. But as the composition of the test cannot be depended on as altogether uniform, we cannot be certain of its accuracy in determining the quantity of iron, and the method is troublesome and complicated, requiring attention to a number of circumstances which influence the result.

The triple prussiate is also, in the common method of preparing it, impure, from a mixture of sulphate of potash derived from the potash of commerce; and this is the source of a mistake, which at one time prevailed among chemists, that barytes is precipitated by this test from its saline solutions. The sulphuric acid may be removed by the action of barytes; a solution of barytes in warm water being added to the liquor prepared by the process described above, as long as a white precipitate ensues.

The prussiate of potash and iron precipitates not only iron from its solution, but the greater number of the other metals, all of them, indeed, except platina, antimony, and tellurium; and this affords a test useful in discovering the metals.

The compound formed from the precipitation of the salts of copper, is of a fine brown colour: it was introduced as a paint by Mr Hatchet, and found superior to any brown paint in use in beauty and intensity. The deepest colour is obtained from the muriate of copper, precipitated by the prussiate of lime and iron; the muriate being dissolved in ten parts of distilled water, and the solution of the prussiate added as long as there is any precipitation *.

Besides the triple compounds of prussic acid, potash, and oxide of iron, other ternary combinations are formed with the other salifiable bases. The prussiate of barytes and iron is crystallizable; the crystals are rhomboidal, and have a yellow colour; they are sparingly soluble in water; four ounces, at 65°, not dissolving more than one grain, and only between five and six grains at 212°. It consists, according to Mr Porret, of barytes 49.1, black oxide of iron 12.42, prussic acid 21.89, water 16.59. The prussiate of strontites and iron is less disposed to crystallize: the dry mass obtained by evaporation is readily soluble in water; one ounce, at 65°, dissolving 120 grains †. The prussiate of lime and iron is deposited, by evaporation of its solution, in minute crystals of a yellowish tinge. The others are scarcely known.

The presence of oxide of iron, it has been remarked, gives more distinctly marked saline properties, and greater permanence of constitution to the combinations into which the prussic acid enters, with the different salifiable bases. Mr Porret conceived the opinion, that these compounds are not, as has been supposed, combinations of prussic acid with a compound base, but that the elements of the prussic acid combine with a certain portion of black oxide of iron, forming a peculiar acid, and this acid unites with the different salifiable bases, forming the compounds which

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* Nicholson's Journal, 4to, vol. iii. p. 171.

† Journals of the Royal Institution, vol. i. p. 306.

have been denominated triple prussiates. In conformity to this, and what he regards as a proof of it, he found, that when these compounds are placed in the voltaic circuit, the prussic acid and oxide of iron pass to the positive pole, and the base to the negative. He endeavoured to procure this acid undecomposed, by dropping into a solution of the triple prussiate of barytes and iron, as much sulphuric acid as was necessary to saturate the barytes. A fluid was thus obtained, which he regarded as the pure acid of the triple prussiates. It was of a pale lemon colour, had no smell, is decomposed by a gentle heat, or by exposure to a strong light, prussic acid being formed, and white triple prussiate of iron; it forms with the alkalis, earths or oxides, the salts named triple prussiates; displaces acetic acid from all its combinations, in the cold; and is capable of expelling all other acids from their soluble combinations, when it can form, with their bases, compounds that are insoluble in acids. It is obvious, that the acidity of this substance in its insulated state, is, from this statement of its properties, problematical; but the hypothesis accounts very well for the effects produced in its combinations, and particularly for the greater permanence of the triple prussiate *; and the discovery of it is interesting, as it had not been before procured. Mr Porret proposed for it the name of Ferruretted Chyazic Acid, and for its saline compounds that of Ferruretted Chazates. Those of Ferro-prussic, and Ferro-prussiates, which have been suggested,

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* This circumstance is ascribed by Gay Lussac, with sufficient probability, to the mutual affinities of the two bases and the acid; and as analogous in this respect to other triple combinations, in which frequently the elements are retained with greater force than in their binary combinations. He gives the example of alumina, with sulphuric acid, in which the combination is less neutral and less permanent, than in that of alumina, potash, and sulphuric acid.

would have been preferable. From his experiments, it appears, that 100 of Ferruretted Chyazic acid consist of 64 of prussic acid, or its elements, and 36 black oxide of iron. Prussic acid, he inferred, consists of carbon 34.8, nitrogen 40.7, hydrogen 24.5. Prussiate of mercury is composed of 13.8 prussic acid, and 86.2 red oxide of mercury: Triple prussiate (ferro-prussiate) of barytes, of barytes 49.10, ferruretted chyazic acid 34.31, (or prussic acid 21.89, black oxide of iron 12.42), and water 16.59: Triple prussiate (ferro-prussiate) of potash, of potash 39.34, ferruretted chyazic acid 47.66, (or prussic acid 30.40, black oxide of iron 17.26), and water 13:—and Blue prussiate of iron, of red oxide of iron 34.235, ferruretted chyazic acid 53.38, (or prussic acid 34.05, black oxide of iron 19.33), and water 12.385 *.

Mr Porret supposed that the property of combining with prussic acid or its elements, so as to increase its acid powers, is not confined to black oxide of iron, but that it belongs to many other bodies. Sulphur, in particular, he inferred, formed a compound of this kind, to which he gave the name of Sulphuretted Chyazic Acid. It may be formed by submitting a prussiate or triple prussiate, to the action of an alkaline sulphuret, or sulphuretted hydro-sulphuret, as well as by various other processes. When obtained pure, it is colourless; of the specific gravity of 1.022; has a pungent smell, resembling that of acetic acid. It consists of 65 of sulphur, and 35 of prussic acid or its elements. With the different bases it forms compounds, named by Mr Porret Sulphuretted Chyazates, many of which are crystallizable, and have the properties of salts.

From the origin of prussic acid, it may be inferred to consist of the elements that usually form the animal products. This is confirmed by the results of its analysis. It was known, that prussian blue, decomposed by heat, af-

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* Philosophical Transactions, 1814, 1815.

fords ammonia; and Scheele found, that ammonia is yielded also by the other prussiates, with carbonic acid gas and residual charcoal. He added an instructive synthetic experiment. Equal parts of charcoal powder and sub-carbonate of potash mixed, were exposed in a crucible to a red heat; he then thrust to the bottom of the crucible nearly the same proportion of muriate of ammonia, in small pieces: in two minutes, the production of ammoniacal vapours had ceased: the matter lixiviated with hot water, afforded a ley, which copiously precipitated prussian blue from sulphate of iron *. A similar, though less perfect result, was obtained when he substituted plumbago. And from these it appears, as he remarks, that volatile alkali, with carbonaceous matter, can afford the acid of prussian blue. No farther inference could be drawn while the nature of ammonia was unknown †.

Berthollet, when he discovered the composition of ammonia, applied it to the theory of the formation of prussic acid. He considered it as a compound of the elements of the ammonia, with a portion of carbon, as a ternary compound therefore of carbon, hydrogen, and nitrogen ‡. The doctrine that oxygen is the principle of acidity, and that all acids contain this element, opposed an objection to this; and some results were stated to prove, that prussic acid contains oxygen, particularly that in the decomposition of a prussiate, such as prussian blue, by heat, however dry it may have been rendered, carbonate of ammonia is a product. But the oxygen necessary to form the carbonic acid, when this product is obtained, Berthollet remarked, is derived from the metallic oxide, which is

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* Chemical Essays, p. 405.

† The same result is obtained when ammoniacal gas is transmitted over ignited charcoal in a tube, as was shewn by Clouet, (Annales de Chimie, tom. xi. p. 30.).

‡ Mémoires de l'Acad. des Sciences, 1786.

the base of the prussiate, and which is more or less reduced. And in confirmation of his theory, he farther adduced the example of sulphuretted hydrogen, as a proof that oxygen is not necessarily required for the constitution of an acid.

Gay Lussac, by more recent investigations *, has fully established this theory, and has determined the precise composition of prussic acid, and presented some very interesting results with regard to it. As it can be made to exist in the gaseous form at a temperature so slightly elevated, he submitted it to analysis by detonating its vapour in Volta's Eudiometer, with oxygen gas. The products are water, carbonic acid, and nitrogen gases. From the quantities, compared with the quantity of oxygen consumed, making a correction for the formation of a small portion of nitric acid, he inferred, that the elements of prussic acid are carbon, hydrogen, and nitrogen, and that these are combined in the proportion of one volume of the vapour of carbon, half a volume of nitrogen, and half a volume of hydrogen, condensed into one volume. To confirm the analysis, he transmitted the vapour of prussic acid over iron wire in an ignited porcelain tube. Two products were obtained,—a gaseous mixture, composed of equal volumes of hydrogen and nitrogen, and charcoal partly deposited on the iron, partly combined with it; results which served to demonstrate, that prussic acid contains equal volumes of hydrogen and nitrogen, and that it contains no oxygen. To determine the quantity of carbon, he passed the prussic acid vapour over brown oxide of copper at a red heat; it was entirely decomposed, the copper was reduced, and water was formed; and the gases disengaged were a mixture of two volumes of carbonic acid and one volume of nitrogen. The volume of carbonic acid

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* Annales de Chimie, vol. xcv. Annals of Philosophy, vol. vii. and viii.

is held to be equal to a volume of the vapour of carbon. Hence these combined results agree with the first analysis in fixing the proportions at one volume of the vapour of carbon, half a volume of hydrogen, and half a volume of nitrogen, condensed into one volume,—and reducing these to weight, 100 of prussic acid consist of carbon 44.39, nitrogen 51.71, hydrogen 3.9. It is peculiarly distinguished, compared with other animal substances, and still more with vegetable products, to which class it also belongs, by the great quantity of nitrogen it contains, the small quantity of hydrogen, and the absence of oxygen *.

From this composition of prussic acid, combined with the analogy which the doctrine of chlorine, and still more the acidity of sulphuretted hydrogen, afforded, it might be inferred to be composed of a compound base, or radical of carbon and nitrogen, combined with hydrogen. Gay Lussac accordingly found, that on heating it with potassium, there is a diminution of volume, and at the same time a production of hydrogen, equal to half the volume of the prussic acid that had disappeared. The compound radical therefore of carbon and nitrogen, had combined with the potassium; and accordingly, on dropping the solid product into water, it dissolved entirely without effervescence, and was converted into simple prussiate of potash; the potassium receiving oxygen from the water so as to form potash, and the hydrogen of this decomposed water re-producing with the prussic radical, prussic acid. By the ac-

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* This determination of the composition of prussic acid is very different from that of Mr Porret before stated, which appears to have been owing to this chemist having over-rated the proportion of hydrogen, by having inferred it from the quantity of oxygen consumed, and having, in the estimate of this, supposed the prussiate of mercury, the form under which he operated on prussic acid, to contain oxygen, while, according to Gay Lussac, it contains none. (Annals of Philosophy, vol. vii. p. 558.).

tion of barytes at a low red heat, and even of potash, and soda, on prussic acid vapour, hydrogen is in like manner separated, and the radical remains in combination with the barytes or the alkaline base.

It was convenient to distinguish this radical by a proper appellation. Gay Lussac adopted that of Cyanogen, derived from the blue colour of its most important and first known product, prussian blue. The acid itself being a compound of cyanogen with hydrogen, he named Hydro-cyanic; its salts, formerly named prussiates, he names hydro-cyanates, and the compounds of cyanogen, he denominated cyanurets.

Gay Lussac succeeded in obtaining cyanogen in an insulated form; an interesting discovery, as the first example of a compound radical having been obtained insulated. The compound considered as prussiate of mercury, prepared by digesting red oxide of mercury with prussian blue, he found reason to conclude, is a cyanuret of mercury, that is, a compound of cyanogen with metallic mercury,—the oxygen of the oxide employed in its formation combining with the hydrogen of the prussic acid, and the cyanogen combining with the metallic quicksilver. When this substance dry is exposed to heat in a retort, it blackens, melts, and yields gas, mercury being also volatilized, and a charry matter remains. This gas is pure Cyanogen. The following are its properties:

It is permanently elastic; its specific gravity to that of air is 1.8064. Its smell is strong and penetrating; its solution in water has a very sharp taste. It bears rather a high temperature without being decomposed; it burns with a bluish purple flame. Water at 68° absorbs about 4½ times its volume; alkohol absorbs 23 times its volume. Sulphuric ether and oil of turpentine, dissolve at least as much as water. It reddens infusion of litmus; on heating the solution, the gas is disengaged, mixed with a little carbonic acid from decomposition of a small portion of cyanogen, and the blue colour is restored. It separates in the dry way their acid from the carbonates. Phosphorus, sulphur, and iodine, are volatilized in it without undergoing any change; nor does it suffer any change from hydrogen at the same temperature, or on passing electric sparks through the mixture. Gold, copper, and platina, are not affected by it at a red heat; but iron, when heated to whiteness, decomposes it in part. Potassium combines with it with incandescence, when a gentle heat is applied. It combines with the alkalis and earths, being absorbed rapidly by their solutions, to which it communicates a yellow or brown colour. The compounds are analogous to salts, and in this respect, as well as in reddening litmus, cyanogen displays the characters of an acid. They are easily decomposed; the addition of an acid causes immediately a production and effervescence of carbonic acid, and at the same time a formation of ammonia, and hydro-cyanic acid. The metallic oxides do not act as the alkalis do; for although the gas is absorbed, hydro-cyanic acid is not formed on the addition of an acid. Cyanogen and ammoniacal gas slowly combine, or at least condense and form a solid brown matter. It unites with sulphuretted hydrogen gas, forming a compound in fine needles, soluble in water, which appears to be the sulphuretted chyazic acid of Mr Porret.

Cyanogen is decomposed by detonation with oxygen; the products are carbonic acid and nitrogen; it is also decomposed by metallic oxides at a red heat. Thus when transmitted over brown oxide of copper at this temperature, it affords the same products, and the oxide is reduced to the metallic form. The proportions of the two gases, taking the mean of the most accurate experiments, are 33.4 measures of nitrogen, and 66.6 of carbonic acid gas,—as nearly as can be expected, one volume of the former and two volumes of the latter. A volume of carbonic acid is equal to a volume of the vapour of carbon. Hence cyanogen consists of 2 volumes of carbon with 1 of nitrogen. And from the density of the cyanogen gas, as well as from the circumstance that the nitrogen obtained is the same in volume as the cyanogen decomposed, it follows that the elements in these proportions are condensed in the combination into one volume. One volume of hydrogen added, forms, as has been already stated, two volumes of hydrocyanic, or prussic acid gas.

Berthollet observed, that prussic acid, when submitted to the action of oxymuriatic acid, suffers a chemical change, and the oxymuriatic passes to the state of muriatic acid. The prussic acid acquires a stronger smell, and appears to exert less energetic affinities to the alkalis: it precipitates iron green from its solutions; and this precipitate becomes blue from exposure to light, or from the action of sulphurous acid, or iron. In this state it has been named Oxyprussic acid. If it be farther impregnated with oxymuriatic acid, and exposed to the light of the sun, it assumes the form of an oily-like matter, of an aromatic odour, which subsides to the bottom of the vessel, and which, if converted into vapour by the application of heat, refuses to unite with water or with oxide of iron.

Gay Lussac found by an examination of the oxy-prussic acid, that it is composed of equal volumes of cyanogen and oxymuriatic acid, or chlorine, and in conformity to the nomenclature suggested by this view, has named it Chloro-cyanic Acid. He obtained it pure by passing a current of oxymuriatic gas through a solution of prussic acid, till the liquor destroyed the colour of a solution of indigo; then removing the excess of oxymuriatic acid by agitation with mercury, and distilling it with a moderate heat, an elastic fluid is disengaged, having the properties of oxy-prussic acid; but it has an intermixture of carbonic acid gas, and when this is removed, it condenses into a liquid, as under the common atmospheric pressure the pure oxy-prussic acid does not remain gaseous at a temperature of 60 or 70.

Chloro-cyanic acid, as Gay Lussac names it, is colourless, and has a very strong pungent smell; it reddens litmus, is not inflammable, and does not detonate when mixed with twice its bulk of oxygen or hydrogen. Its aqueous solution does not precipitate nitrate of silver, nor barytic water. The alkalis absorb it rapidly, and an excess of them is necessary to destroy its odour. On adding an acid to these compounds, the chloro-cyanic acid is decomposed, a strong effervescence of carbonic acid is produced, ammonia is formed, and muriatic acid remains. Gay Lussac endeavoured to perform its analysis by detonating the elastic fluid in which it exists mixed with carbonic acid, with oxygen, and a small addition of hydrogen, to excite the combustion. The carbonic acid gas produced, he found equal to the volume of chloro-cyanic acid, the nitrogen which was the other elastic product, equal to half its volume: it contains, therefore, he inferred, 1 volume of vapour of carbon, and half a volume of nitrogen; from some indirect considerations, he farther concluded, that it contains half a volume of chlorine: and these elements, he lastly inferred, are condensed into half of the sum of their volumes. The proportions of the elements thus assigned, come to the same as equal volumes of cyanogen and chlorine, united without any condensation. Hydro-cyanic acid in like manner consists of equal volumes of cyanogen and hydrogen, so that the constitution of these two compounds is according to this view similar, with the substitution of chlorine in the one, for hydrogen in the other. Much of this, however, can scarcely be considered as the direct inference of very rigid experimental results.

SECT. II.—OF THE SPONTANEOUS DECOMPOSITION OF ANIMAL SUBSTANCES AT LOW TEMPERATURES.

WHEN the affinities of the elements of dead animal matter are allowed to operate by that degree of humidity or softness which these substances usually have, new combinations are established even at natural temperatures, which continue to proceed until the animal substance is entirely decomposed. Changes of this kind constitute the general process of Putrefaction; though they are also considerably varied, according to the circumstances under which they take place, and, in particular, according to the presence of air and humidity.

If animal matter be entirely excluded from these two agents, in other words, if it be completely dried and secluded from the atmosphere, it decays very slowly, any sensible chemical decomposition not being produced in it for a very great number of years; and by complete desiccation, animal matter may be preserved almost for an indefinite time.

If those animal substances which are not soluble in water, those, for example, which consist principally of fibrin, as the muscular fibre or flesh, be kept compressed, or be immersed in water, as the air is thus nearly excluded, the series of changes are modified, and the fibrin is ultimately converted into a fatty substance, having properties similar to those of spermaceti; and to which, as being in some measure intermediate between fat and wax, Fourcroy gave the name of Adipocire.

This species of decomposition was first particularly observed on the occasion of the removal of a burying-ground in Paris, containing common graves, or receptacles destined for the poor, in which a number of bodies were accumulated together, and afterwards covered with earth. It was known to the grave-diggers, that after a number of years they were converted into a species of fatty matter. Fourcroy examined the appearances presented, and gave a memoir on the subject *. The change was found to take place very gradually. The humours of the body first appeared to pass into putrefaction, the products of which would escape chiefly in the gaseous form. The more solid matter underwent a slower decomposition, the first product of which appeared to be principally ammonia, which combining with the altered fibrin formed a species of soap. The transition of the fibrin towards a species of fat continued to proceed: the ammonia seemed at the same time to escape, or to be decomposed, and at length the residue was converted into the unctuous product named Adipocire. This substance was considered as a peculiar product of decomposition, uniform and homogeneous. But, according to Chevreul, it is a species of soap, formed of margaric acid with liquid fat. It has been shewn by Dr Gibbes, that when the flesh of animals is immersed under water, it is converted into a similar substance: in a piece of lean beef, secured in a running stream, the conversion was effected in the course of a few months; and it was also produced by the agency of dilute nitric acid †. In these changes, part of the nitrogen and hydrogen appear to combine and form ammonia, while another portion of hydrogen with carbon, and a portion of oxygen, form the residual matter.

When the atmospheric air is not entirely excluded, and moisture is present, the process more strictly named Putrefaction takes place. This has been defined, that species of

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* Annales de Chimie, tom. v. p. 154.

† Philosophical Transactions, 1794, 1795.

decomposition or change in the mixture of organic matter, by which ammonia and a particular effluvium of a most offensive smell, called Putrid, are formed. It takes place only in those substances which, besides carbon and hydrogen, contain nitrogen and phosphorus: such are the animal products and vegetable gluten. The circumstances more peculiarly favourable to it, are a due degree of heat and moisture, and the access of air.

The temperature which is most favourable to putrefaction, is that from 60 to 80. Too high a heat retards it, by dissipating humidity; cold checks it, by increasing that cohesion which counteracts chemical action; and it completely prevents it, when the temperature is such as to produce congelation.

Communication with the atmosphere is necessary to admit of the formation and escape of the elastic products; the presence of the air too, to a certain extent, favours the change, apparently by the action of oxygen. Hence putrefaction is retarded in an atmosphere of carbonic acid gas. On this is founded the process of Appert, for preserving animal and vegetable substances from putrefaction, and which affords at once the best proof and illustration of the fact. The process consists in inclosing the substances in bottles or jars, which being filled are corked very closely, and a lute applied over the cork, composed of cheese and lime, which hardens speedily, and if well applied prevents effectually any admission of the air. The bottles thus prepared are placed in water, which is then heated up to the boiling point, and they are subjected to this temperature for a certain time, longer or shorter according to the kind of matter operated on. While the air remains excluded, the substance remains perfectly unchanged, and may thus be preserved for months or years; but if admitted even in small quantity, if the luting or cork, for example, is in the slightest degree defective, it is soon tainted. The small portion of air found in the bottles after the operation, is found deprived of oxygen.

In this process, too, is displayed a singular and important fact with regard to the agency of oxygen in putrefaction. The bottles being closed previous to the exposure to heat, must necessarily contain with the included matter a portion of air; and if heat were not applied, or even if applied imperfectly, putrefaction would take place. This proves that the effect of the high temperature is to produce some kind of combination of the oxygen of the air with the animal or vegetable matter, not leading to putrefaction, or even counteracting it, while by this combination it is effectually removed. The air accordingly, where the process is successful, is deprived of oxygen; but if the heat were not sufficiently prolonged, and all the oxygen of the air in the bottles not exhausted, putrefaction soon came on. If the bottles were opened only for a short time and again closed, without heat being applied, the inclosed substances soon putrefied: as they did also from mere exposure to the air. But if, after having been exposed even for an hour or two, they were re-placed, the vessels again accurately closed, and then the due degree of heat applied, they could be preserved as at first. And this repeated exposure to the air, and removal of its operation by heating, it appears from Gay Lussac's experiments, can be renewed a number of times. Nay, by occasional exposure to the heat of boiling water, without the exclusion of the air, he found the exemption from putrefaction to be attained. It is in consequence of this, that Appert's method is so much more successful than that which had been before used, of closing the vessels after heat had been applied; for although in the latter mode the interposed air might be expected to be more effectually expelled, still the portion which entered again before the closing could be completed was sufficient, when its effect remained uncounteracted by heat, to excite the putrefactive change. The theory of these effects is not very apparent. Gay Lussac supposes, that the oxygen may combine with that principle analogous to gluten, which excites fermentation, and which may equally excite putrefaction; that this by a kind of coagulation is separated by heat, and thus rendered inert; and that it is only that part of it which has suffered oxygenation which is capable of this coagulation; it is thus removed, while the exclusion of oxygen prevents the putrefaction from taking place, which would otherwise be excited by the remainder. But this is rather hypothetical and unsatisfactory. And indeed the theory of the operation of antiseptics is altogether imperfectly understood. Substances of the most discordant kind, alkohol, aromatics, sugar, salt, are all employed with more or less success; and it is difficult to conceive of any common agency by which their effects can be explained; or with regard to some of them, common salt for example, of any operation whatever by which they should be capable of counteracting the changes which constitute putrefaction *.

When putrefaction commences, the matter emits a slightly offensive smell, which soon becomes extremely fœtid; the taste becomes nauseous: the colour is greenish: the firmness and cohesion of the substance are also diminished, and at length it becomes soft and pulpy; its smell becoming more and more offensive. It thus continues, losing weight, until the decomposition is completed, and little remains but an earthy residuum.

In this process, the putrefying matter is resolved into new compounds, which escape in the gaseous form. The

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* Appert on Preserving Animal and Vegetable Substances; also Memoir, Annales de Chimie, tom. xlvi.; or Nicholson's Journal, vol. vii. Memoir by Gay Lussac, Nicholson's Journal, vol. xxxi.

precise nature of these combinations has not, from the offensiveness of the process, been very accurately ascertained, and they probably vary somewhat according to the nature of the animal substance, and the circumstances under which the putrefaction takes place. A few experiments with regard to them were made by Guyton *. Ammonia is formed by the union of the nitrogen and hydrogen of the animal matter; it appears to be one of the first products, and it is often accompanied by a production of acetic acid, by which it is neutralized; hence Guyton found, that the effluvia from a putrid substance indicated no presence of ammonia by the most delicate vegetable colours; but unequivocal signs of it were afforded, on exposure to the vapour arising from the action of lime on water which had been exposed to the action of these effluvia. Carbonic acid gas seems to be formed in every stage of the process; it is easily detected in considerable quantity by the effect on lime-water, and seems to constitute the chief part of the elastic product. Phosphuretted hydrogen appears to be disengaged, since this gas, even when obtained pure, has very perceptibly the odour more peculiarly putrid; or perhaps phosphorus may be disengaged in combination with nitrogen, giving this odour. Sulphuretted hydrogen makes another part of the vapours disengaged from putrefying substances; as these vapours have in some degree its smell, and are capable of blackening the metals, a peculiar property of this gas. The air over putrid matter, Guyton found, produced a dark-coloured pellicle and precipitate from solutions of silver and lead. It is probable too, that not only these binary combinations, but compound gases, consisting of three or more of these elements with oxygen, are formed and disengaged. The putrid odour seems to arise from a minute portion of matter which

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* Treatise on the Means of Purifying Infected Air, p. 75.

is volatile, and which is capable of being diffused through aeriform fluids, or slightly combined with them.

This change, then, consists in the elements of the animal substance entering into new combinations, which pass off in the gaseous form, the earthy and saline matter forming the residuum.

Putrefaction is the great process employed by nature, to separate the principles which vegetation and animalization had combined, to restore the elements of bodies to their simpler forms, and thus to be subservient to their recomposition. It is a process which necessarily goes on at the surface of the earth; its products are diffused through the atmosphere, absorbed by water, or form part of the soil. They furnish the principal nutritious matter for the support and growth of vegetables, and they are thus again brought into new combinations, which are prepared for assimilation in the animal system.

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